

**REMARKS/ARGUMENTS**

**A. Status of the Claims**

Claims 22-24, 28-40, 42, 43 and 47-49 were pending at the time the Action was mailed. Claims 28 and 47 are amended to correct grammatical errors. Claim 49 is amended, as described below. No new matter is introduced by these amendments. Claims 22-24, 28-40, 42, 43 and 47-49 are pending.

**B. The Indefiniteness Rejection Is Overcome**

Claim 49 is rejected under 35 U.S.C. § 112, second paragraph, as being indefinite regarding a grammatical error. Claim 49 is amended to address this error. Withdrawal of the rejection is respectfully requested.

**C. The Genera of ( $\alpha,\omega$ )-Diol and -Dithiol Polysulfide Prepolymers Are Enabled**

Claims 22-24, 29-35, 38, 40, 42, 43, 47 and 49 are rejected under 35 U.S.C. § 112, first paragraph, as failing the enablement requirement. The Examiner contends that while the specification is enabling for making and using polysulfide containing ( $\alpha,\omega$ )-dithiol prepolymers according to those set forth at pages 4, 5 and 10-19 of the specification, it does not reasonably provide enablement to make and use “virtually any polysulfide containing ( $\alpha,\omega$ )-diol prepolymers or polysulfide containing ( $\alpha,\omega$ )-dithiol prepolymers.” Action, p 2.

**1. Summary of the Argument**

“The test of enablement is whether one reasonably skilled in the art could make or use the invention from the disclosures in the patent coupled with information known in the art without undue experimentation.” See MPEP § 2164.01 (citing *United States v. Telectronics, Inc.*, 857 F.2d 778, 785 (Fed. Cir. 1988)). The specification, combined with the knowledge available to those of skill in the art, enables skilled artisans to both make and use an “( $\alpha,\omega$ )-diol or -dithiol

prepolymer, said ( $\alpha,\omega$ )-diol or dithiol prepolymer being a polysulfide or a mixture of polysulfides,” as claimed.<sup>1</sup> *Id.*

First, the Examiner fails to properly support the enablement rejection with respect to how to make ( $\alpha,\omega$ )-dithiol polysulfide prepolymers, such that Applicant is under no obligation to provide proof of enablement of these compounds. Despite this, Applicant shows that not only are sufficient examples of how to make these dithiol prepolymers described in the specification to enable the claimed genus, but the prior art provides numerous examples of how to make both ( $\alpha,\omega$ )-diol and -dithiol polysulfide prepolymers. Thus, a skilled artisan would not have to undertake undue experimentation to produce either of these prepolymers.

Second, the Examiner also fails to properly support the enablement rejection with respect to how to use ( $\alpha,\omega$ )-dithiol polysulfide prepolymers. Despite the lack of Applicant's obligation to prove enablement in view of this deficiency, Applicant shows that information provided in the specification in this regard, including at least one working example, enable the claimed genus. Moreover, one of skill in the art would recognize that the claimed ( $\alpha,\omega$ )-diol polysulfide prepolymers may be used in the same way as the claimed and enabled ( $\alpha,\omega$ )-dithiol polysulfide prepolymers, such that the use of ( $\alpha,\omega$ )-diol polysulfide prepolymers is also enabled.

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<sup>1</sup> For ease of language, Applicants refer to these classes of prepolymers as “( $\alpha,\omega$ )-diol polysulfide prepolymers” and “( $\alpha,\omega$ )-dithiol polysulfide prepolymers.”

**2. The Specification Enables A Skilled Artisan As To How To Make ( $\alpha,\omega$ )-Dithiol and Diol Polysulfide Prepolymers**

**a. *The Examiner has failed to properly support the enablement rejection of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers regarding their production***

The Examiner contends that the specification provides no guidance as to how to produce ( $\alpha,\omega$ )-dithiol polysulfide prepolymers, other than with respect to those described at pages 4, 5 and 10-19 of the specification. Action, pp 2, 3 and 5. Thus, the Examiner concedes that the ( $\alpha,\omega$ )-dithiol polysulfide prepolymers described in these pages are enabled. *See id.* at p 2. However, the Examiner offers only conclusory allegations that these examples fail to enable the claimed genus. This legal insufficiency alone renders the enablement rejection improper:

[I]t is incumbent upon the Patent Office, whenever [an enablement rejection] is made, to explain *why* it doubts the truth or accuracy of any statement in a supporting disclosure and to back up assertions of its own with acceptable evidence or reasoning which is inconsistent with the contested statement.

MPEP § 2164.04 (citing *In re Marzocchi*, 439 F.3d 220, 224 (CCPA 1971)) (emphasis in original). No such explanations, evidence or reasoning is presented.

The MPEP further states that Applicant is under no obligation to prove enablement under these circumstances:

Proof of enablement will be required for other members of the claimed genus only where adequate reasons are advanced by the examiner to establish that a person skilled in the art could not use the genus as a whole without undue experimentation.

MPEP § 2164.02. Despite this lack of obligation, Applicant provides the following arguments to show that the specification enables the claimed genus of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers.

**b. The examples of ( $\alpha,\omega$ )-dithiol polysulfide prepolymer preparations described in the specification enable the claimed genus**

The preparations of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers described on pages 4 and 5 of the specification, which the Examiner states are enabled, also enable the claimed genus. See MPEP § 2164.01(b) (as long as the specification discloses at least one method for making and using the claimed invention that bears a reasonable correlation to the entire scope of the claim, then the enablement is satisfied) (citing *In re Fisher*, 427 F.2d 833, 839 (CCPA 1970)).

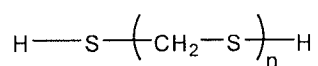
Page 4 of the specification states that ( $\alpha,\omega$ )-dithiol polysulfide prepolymers of formula (Ia) “can be made by polymerizing sulfide monomers, such as ethylene sulfide and 2-mercaptoethyl sulfide (DMES).” Further, ( $\alpha,\omega$ )-dithiol polysulfide prepolymers may “[result] from the polymerization of diepisulfides of formula... (Ib).” *Id.* Spanning pages 4 and 5 of the specification is a description of how to prepare ( $\alpha,\omega$ )-dithiol polysulfide prepolymers of formula (Ic): “thermal and/or photopolymerization, in the presence of an initiator, of 2-mercaptoethylsulfide (DMES)... and allylsulfide....” Thus, pages 4 and 5 of the present specification provide at least three methods of making three classes of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers. Furthermore, the specification provides working examples of how to prepare ( $\alpha,\omega$ )-dithiol polysulfide prepolymers. For example, allylsulfide and 2-mercaptoethylsulfide were combined in ***at least 22 different ways*** to produce various ( $\alpha,\omega$ )-dithiol polysulfide prepolymers. Specification, pp 10-19. These multiple examples provide ample guidance to a skilled artisan as to how to make the claimed genus of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers. See MPEP § 2164.02 (“For a claimed genus, representative examples together with a statement applicable to the genus as a whole will ordinarily be sufficient if one skilled in the art... would expect the claimed genus could be used in that manner without undue experimentation.”).

To further establish that the production of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers is enabled, Applicant includes a Declaration of Aref Jallouli, Ph.D., who is one of the co-inventors of the present application. Dr. Jallouli is an experienced polymer science and materials science researcher who is familiar with monomers, polymers, polymerizable compositions and materials for ophthalmic glasses. Declaration, pp 1-2. Dr. Jallouli confirms the evidence discussed above, stating that ( $\alpha,\omega$ )-dithiol polysulfide prepolymers are "easily synthesizable without undue experimentation from readily available starting materials using known procedures." Declaration, p 2. This evidence further establishes that a skilled artisan would be able to make the claimed ( $\alpha,\omega$ )-dithiol polysulfide prepolymers, and that the specification is enabling in this regard.

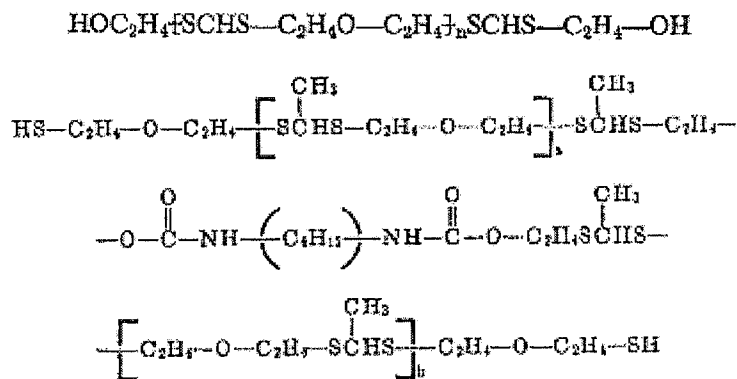
***c. The prior art contains numerous examples of the preparation of ( $\alpha,\omega$ )-diol and -dithiol polysulfide prepolymers***

In contending that the scope of prior art regarding the claimed invention is limited to WO 01/36507 and WO 01/36508, the Examiner asserts that nothing in these documents teaches one how to make the claimed ( $\alpha,\omega$ )-diol and dithiol polysulfide prepolymers. Action, pp 3-4. The Examiner further asserts that general knowledge available to skilled artisans is insufficient to allow others to make either of the claimed prepolymers. *Id.* at p 4. Applicant provides evidence that contradicts each of these statements.

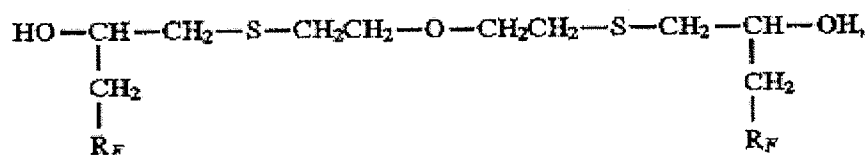
The scope of prior art with respect to the production of ( $\alpha,\omega$ )-dithiol and -diol polysulfide prepolymers is not limited to the two international applications cited by the Examiner. Numerous examples exist in literature that pre-date Applicant's filing date that describe making these compounds. For example, U.S. Patent 3,056,841 describes dithiol poly(alkylene sulfide) prepolymers of the following formula, and syntheses thereof:



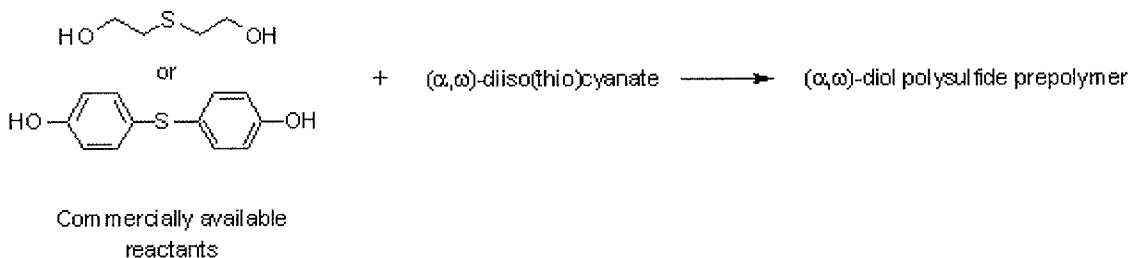
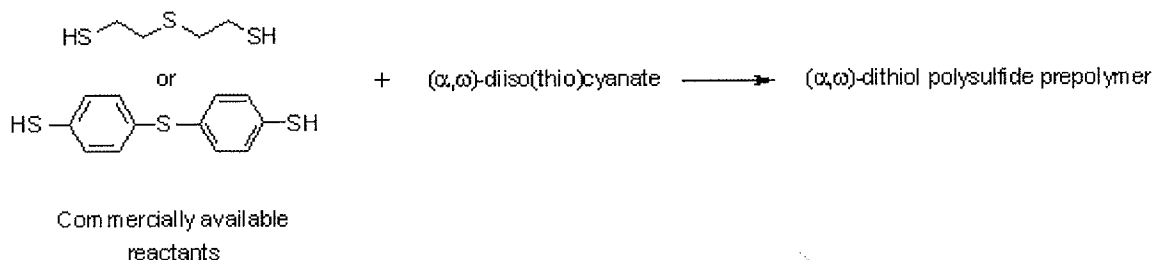
'841 patent, col. 32, line 36 (Appendix A). U.S. Patent 3,413,265 provides additional examples and methods of making the claimed prepolymers, such as the compounds shown below:



'265 patent, col. 10, line 75; and col. 11, lines 30-40 (Appendix B). Diols of the following formula are also shown in U.S. Patent 5,708,119 at col. 14, line 30 (Appendix C), along with methods of their preparation:



Finally, knowledge commonly available in the art of polymer chemistry allows skilled artisans to synthesize ( $\alpha,\omega$ )-dithiol and -diol polysulfide prepolymers as presently claimed. For example, reaction of a diisocyanate with an excess of diol or dithiol monomer in accordance with the schemes shown below yields prepolymers as claimed.



These types of reactions are well within the scope of knowledge of skilled artisans. For example, polymerization reactions of diol and dithiol functionalities are described in several reference books, including H. Ulrich, "Chemistry and Technology of Isocyanates," Wiley, New York, 1996.

Finally, Dr. Jallouli confirms that (α,ω)-dithiol polysulfide prepolymers are "classical compounds" (*i.e.*, well-known) that "have been known for years." Declaration, p 2. Dr. Jallouli also explains that the preparation of (α,ω)-diol polysulfide prepolymers is not burdensome. *Id.* Further, various (α,ω)-diol and -dithiol polysulfide prepolymers are commercially available.

#### ***d. Conclusion***

Not only is the Examiner's legal reasoning insufficient to support the enablement rejection regarding how to make (α,ω)-dithiol polysulfide prepolymers, evidence discussed above negates any assertion that the production of either (α,ω)-diol or -dithiol polysulfide prepolymers is not enabled by the specification in combination with knowledge available to

skilled artisans. Thus, to the extent the enablement rejection is based on a lack of teaching by the specification or the art regarding making these prepolymers, the rejection is improper.

**3. The Specification Enables A Skilled Artisan As To How To Use ( $\alpha,\omega$ )-Diol and -Dithiol Polysulfide Prepolymers**

***a. The Examiner fails to properly support the enablement rejection of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers regarding their use***

The legal deficiencies described above regarding the Examiner's assertion that the genus of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers is not enabled regarding their production may also be relied upon to counter the Examiner's assertion regarding the alleged lack of enablement regarding the use of these compounds. As noted above, the Examiner admits that the ( $\alpha,\omega$ )-dithiol polysulfide prepolymers on pages 4, 5 and 10-19 of the specification are enabled. However, the Examiner offers no explanations, evidence or reasoning to support the contention that the examples of uses of these prepolymers insufficiently enable the claimed genus. The enablement rejection is therefore legally improper in this regard. *See* MPEP § 2164.04. Despite the lack of obligation on Applicant's part to prove enablement under these circumstances (*see* MPEP § 2164.02), Applicant provides the following arguments to establish that the specification enables the claimed genus of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers with respect to their use.

***b. The examples of uses of ( $\alpha,\omega$ )-dithiol polysulfide prepolymer described in the specification enable the claimed genus***

The uses of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers described on pages 4, 5 and 10-19 of the specification, which the Examiner states are enabled, also enable the claimed genus. *See* MPEP § 2104.01(b) (citing *In re Fisher*, 427 F.2d 833, 839 (CCPA 1970)) (as long as the specification discloses at least one method for making and using the claimed invention that bears a reasonable correlation to the entire scope of the claim, then the enablement is satisfied).



( $\alpha,\omega$ )-Dithiol polysulfide prepolymers are described on page 3 of the specification as reagents that, in combination with an iso(thio)cyanate, produce ( $\alpha,\omega$ )-diiso(thio)cyanate polysulfide prepolymers. This use is commensurate in scope with claim 22. As discussed above in sections (2)(b) and (c), incorporated herein, numerous examples of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers are provided both in the specification and in the art. Skilled artisans were generally aware, at the time of the filing of the present specification, that dithiols could be used as reactants along with iso(thio)cyanates in polymerization reactions. *See* H. Ulrich, "Chemistry and Technology of Isocyanates," Wiley, New York, 1996. Indeed, the level of skill in the art in this regard is high, and all of the methods needed to practice the invention in this regard were well known to skilled artisans.

Moreover, at least one working example of a use of particular ( $\alpha,\omega$ )-dithiol polysulfide prepolymers is described at pp 19-24 of the present specification that is commensurate in scope with the claimed invention. There is nothing to suggest that the claimed genus of dithiol polysulfide prepolymers is not enabled in view of this working example combined with knowledge available to skilled artisans. *See* MPEP § 2164.02 (regarding the evaluation of a single working example in an application, an examiner must "evaluate all the facts and evidence and state why one would not expect to be able to extrapolate that one example across the entire scope of the claims"). *See also id.* ("For a claimed genus, representative examples together with a statement applicable to the genus as a whole will ordinarily be sufficient if one skilled in the art... would expect the claimed genus could be used in that manner without undue experimentation.").

Finally, Dr. Jallouli confirms that all of the examples of ( $\alpha,\omega$ )-dithiol polysulfide prepolymers discussed in the specification are representative of the genus as a whole.

Declaration, p 2. Dr. Jallouli states that a skilled artisan would be able to use the claimed genus of  $(\alpha,\omega)$ -dithiol polysulfide prepolymers in view of such examples. *Id.*

In view of the above, there is no reason to believe that the claimed scope of  $(\alpha,\omega)$ -dithiol polysulfide prepolymers described in the specification cannot be employed as claimed. Accordingly, the genus of  $(\alpha,\omega)$ -dithiol polysulfide prepolymers is enabled.

*c. Use of  $(\alpha,\omega)$ -diol polysulfide prepolymers is enabled*

Since the use of  $(\alpha,\omega)$ -dithiol polysulfide prepolymers is enabled, it cannot be said that the use of  $(\alpha,\omega)$ -diol polysulfide prepolymers is not enabled. The Federal Circuit has had the opportunity to decide a number of enablement issues. In *AK Steel Corp. v. Sollac*, 344 F.3d 1234, 1244 (Fed. Cir. 2003) (internal citation omitted), for instance, the Court stated:

[T]he applicant's specification must enable one of ordinary skill in the art to practice the full scope of the claimed invention.... That is not to say that the specification itself must necessarily describe how to make and use every possible variant of the claimed invention, for the artisan's knowledge of the prior art and routine experimentation can often fill gaps, interpolate between embodiments, and perhaps even extrapolate beyond the disclosed embodiments, depending upon the predictability of the art.

Due to the similar nature of diols and dithiols,  $(\alpha,\omega)$ -diol polysulfide prepolymers are enabled by the specification in combination with information known to those of skill in the art in the same respect as the claimed  $(\alpha,\omega)$ -diol polysulfide prepolymers.

Persons of skill in the art understand that alcohol and thiol functional groups often behave similarly. This common behavior stems from the fact that oxygen and sulfur are members of the same family of elements; therefore, they share similar properties. Zumdahl, S. S., "Chemistry," 3<sup>rd</sup> ed., D.C. Heath and Co., Lexington, Mass., pp 58-60, 1993 (Appendix D). As oxygen and sulfur behave similarly, alcohol and thiol groups behave similarly. Vollhardt and Schore, "Organic Chemistry," 2<sup>nd</sup> ed., W.H. Freeman and Co., New York, 1994, p 306 (Appendix E).

Accordingly, due to their diol and dithiol groups,  $(\alpha,\omega)$ -diol polysulfide prepolymers share similar structural features with  $(\alpha,\omega)$ -dithiol polysulfide prepolymers. These similar features also relate to the use of these compounds as reagents in producing the claimed diiso(thio)cyanate polysulfide prepolymers. For example, attached to each of the chemically similar oxygen and sulfur atoms of the diol and dithiol end groups of these prepolymers is a labile hydrogen atom. These end groups are capable of polymerizing in the presence of at least one cycloaliphatic or aromatic diiso(thio)cyanate as claimed to yield a common product: an  $(\alpha,\omega)$ -diiso(thio)cyanate polysulfide prepolymer. *See* specification, p 3. Moreover, each of the prepolymers comprise a polysulfide moiety that contributes to obtaining a high refractive index material when used in the claimed methods. *Id.* This polysulfide moiety is another common structural feature between the claimed diol and dithiol prepolymers that speaks to the similar uses of these compounds.

Dr. Jallouli also confirms that, in view of the discussion of  $(\alpha,\omega)$ -dithiol polysulfide prepolymers in the specification, a skilled artisan would find  $(\alpha,\omega)$ -diol polysulfide prepolymers enabled by the specification in combination with knowledge available to those of skill in the art. Declaration, p 2. Dr. Jallouli's reasoning is based on the fact that "the use of diol compounds is a conventional alternative to the use of dithiol compounds for a person skilled in the art of polymer chemistry." *Id.*

Since  $(\alpha,\omega)$ -dithiol polysulfide prepolymers are enabled, as explained above,  $(\alpha,\omega)$ -diol polysulfide prepolymers are also enabled as both types of prepolymers are chemically similar and may be used in similar ways. Indeed, there is no reason to believe that diol groups would behave any differently than the dithiol groups in these polymers such that the diol prepolymers could not be used in the same way as the dithiol prepolymers. Therefore, in view of the enabled

teachings of the specification and the art regarding  $(\alpha,\omega)$ -dithiol polysulfide prepolymers, this genus is also enabled.

***d. Conclusion***

Not only is the Examiner's legal reasoning insufficient to support the enablement rejection regarding the use of  $(\alpha,\omega)$ -dithiol polysulfide prepolymers, evidence discussed above negates any assertion that the use of either  $(\alpha,\omega)$ -diol or -dithiol polysulfide prepolymers is not enabled by the specification in combination with knowledge available to skilled artisans. Thus, to the extent the enablement rejection is based on a lack of teaching in the specification or the art regarding the use of these prepolymers, the rejection is improper.

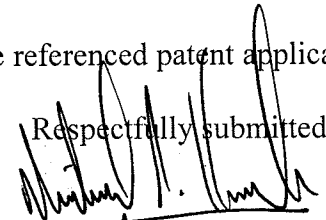
**D. Claim 47 Is Improperly Included In the Enablement Rejection**

As a final point, claim 47 is improperly rejected. The "polysulfide or mixture of polysulfides" of this claim are examples of  $(\alpha,\omega)$ -dithiol polysulfide prepolymers found on pages 4 and 5 of the specification. The Examiner states that  $(\alpha,\omega)$ -dithiol polysulfide prepolymers on these pages are enabled. Action, p 2. Thus, rejection of this claim is improper. Withdrawal of the rejection of this claim is respectfully requested.

**E. Conclusion**

Applicants believe that the present document is a full and complete response to the Office Action mailed March 21, 2008. The present case is in condition for allowance and such favorable action is requested.

The Examiner is invited to contact the undersigned Attorney at (512) 536-3015 with any questions, comments or suggestions relating to the referenced patent application.

Respectfully submitted,  
  
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Date: September 22, 2008

Appl. No. 09/992,054  
Response to Office Action  
Mailed March 21, 2008

## **APPENDIX A**

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3,056,841

## PROCESS FOR PREPARING MERCAPTO-TERMINATED THIOMETHYLENE COMPOUNDS

Klaus A. Saegebarth, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware  
No Drawing. Filed Sept. 6, 1961, Ser. No. 136,207  
7 Claims. (Cl. 260-609)

This invention relates to a novel process for preparing methane dithiol and low molecular weight mercapto-terminated polythiomethylenes and more particularly to a process for preparing these materials from hydrogen sulfide and formaldehyde.

Methane dithiol and mercapto-terminated polythiomethylenes are highly desirable materials. The polythiomethylene compounds made by the process of the present invention are useful at temperatures up to about 200° C. as lube oil additives in which they act both as antioxidants and as lubricity improvers.

The polythiomethylenes and methane dithiol have reactive —SH groups and are thus useful chemical intermediates. They can be reacted with NCO-terminated polymers or organic polyisocyanates to make polythiourethanes which exhibit excellent oxidative and thermal stability. The polythiourethane reaction products are useful for fabricating a wide variety of plastic and elastomeric articles. Furthermore, cellular products, suitable for making crash pads, topper pads, resilient cushions, rigid insulation panels, and the like, result when gas or a gas-forming agent is incorporated for expanding the reaction product prior to cure.

Although procedures for the preparation of methane dithiol and mercapto-terminated polythiomethylenes have been reported, the yields are not entirely satisfactory.

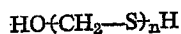
It is an object of the present invention to provide an improved process for preparing methane dithiol and low molecular weight mercapto-terminated polythiomethylenes. A further object is to provide a process for preparing these materials from readily available inexpensive starting materials. Other objects will appear hereinafter.

These and other objects of this invention are accomplished by providing a process for preparing methane dithiol and mercapto-terminated polythiomethylenes which comprises (a) reacting 1.75 to 10 mols of hydrogen sulfide as a liquid with about one mol of formaldehyde at superatmospheric pressure and at temperatures between about 40° C. and 150° C. so as to produce a normally liquid intermediate whose infrared absorption spectrum indicates the presence of mercapto and hydroxyl groups; (b) contacting said intermediate with an aqueous non-oxidizing mineral acid at a temperature of about 25° C. to 175° C., at least until the infrared absorption characteristic of the hydroxyl group disappears; and (c) recovering the bis-mercaptan thereby formed which has the structure



where  $n$  is an integer of at least 1 indicating a number-average molecular weight up to about 160. If desired, the bis-mercaptan may be contacted with water at about 100° C. to increase the number-average molecular weight of the bis-mercaptan up to about 350.

The present process is carried out in several steps. In the first step, hydrogen sulfide is reacted with formaldehyde to obtain a normally liquid intermediate whose infrared spectrum contains bands at 3.95 and 3.0 microns characteristic of mercapto and hydroxyl groups, respectively. It is believed that at least part of the hydroxyl groups are present in molecules having the structure

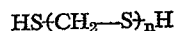


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This reaction is to be carried out at temperatures ranging from about 40° to 150° C. and at superatmospheric pressure. If desired, the hydrogen sulfide may be initially reacted with the formaldehyde at temperatures lower than about 40° C.; however, it is necessary, in order to obtain the bis-mercapto compound, that the reaction be completed by heating to temperatures within the 40° to 150° C. range. The reaction time may range from about 1 to 6 hours. It has been found that the higher the reaction temperature and the longer the reaction time, the higher the molecular weight of the thiomethylene compound obtained. It is necessary that the reaction be carried out at superatmospheric pressure, usually autogenous pressure. It is essential that the pressure be sufficiently above atmospheric to liquefy the hydrogen sulfide.

The amount of hydrogen sulfide employed for reaction with the formaldehyde should range from about 1.75 to 10 moles per mole of formaldehyde. The formaldehyde may be used as an aqueous solution (such as a 37% aqueous solution stabilized with 12% methanol); however, quite satisfactory results are obtained when paraformaldehyde itself is used. The preferred ratio of reactants is about 1.75 to 2 moles of hydrogen sulfide per mole of formaldehyde. Other conditions being held constant, the molecular weight of the thiomethylene compound obtained tends to decrease as the value of the molar ratio of hydrogen sulfide to formaldehyde increases.

It is not necessary to isolate the normally liquid intermediate which is obtained as a result of the first step of the process. After it has been formed and the excess hydrogen sulfide has been removed by application of heat and vacuum, the intermediate is then contacted with an aqueous non-oxidizing mineral acid and thereby converted to the bis-mercaptan having the structure



Suitable non-oxidizing acids include sulfuric, which is preferred, and hydrochloric acid. Representative and preferred concentrations are about 4 to 6 N.

This reaction with the acid can be carried out at any temperature ranging from about 25 to 175° C. At temperatures below 25° C. the reaction rate is too slow for the usual convenience. At temperatures above 175° C. there is an increased possibility of damaging the product as well as causing undesired polymerization to occur giving rise to crystalline high molecular weight products. In general, it is preferred to operate this step of the present process at about 100° C.

The pH of the medium in which the bis-mercapto compound is formed can influence the molecular weight. If the heating is carried out at a pH of 7 (neutral), the molecular weight of the bis-mercapto compound rises. For example, a fluid bis-mercapto compound having a molecular weight of 155 was changed by heating at 100° C. in water (pH of 7) to a benzene soluble higher analog having a molecular weight of 300 and melting at 50-55° C. Heating with water thus provides a way of obtaining tractable higher molecular weight polymers.

The concentration of the mineral acid in the aqueous phase can vary over a quite wide range without unduly affecting the molecular weight of the bis-mercaptan obtained. In a representative example of the preferred procedure, a hydroxy-mercapto-liquid intermediate having a molecular weight of 146 was prepared at 60° C. over a period of 4 hours; the pH of the aqueous solution at this point was 3.5-4. After the solution had been made 6 N in sulfuric acid and heated at 100° C. for six hours under a nitrogen atmosphere, a mercapto-terminated polythiomethylene was obtained having a molecular weight of 152. The polymer which was heavier than water and

completely insoluble in water, was drawn off from the bottom of the reaction vessel.

After the liquid intermediate has been converted to the bis-mercaptan, it is merely necessary to recover this latter material from the reaction mixture by conventional means. If desired, the present invention may be operated on a continuous basis. Thus, formaldehyde, hydrogen sulfide and water may be continuously introduced into the upper portion of a well-agitated reaction zone. The hydroxy-mercapto liquid intermediate formed therein is then withdrawn from the base of this reaction zone and sent to a second reaction zone where hydrogen sulfide is continuously removed and recycled to the first reaction zone. The solution of the liquid intermediate is continually acidified by the addition of the non-oxidizing acid and the bis-mercaptan is continually withdrawn from the bottom of the reaction zone.

The following examples will better illustrate the nature of the present invention; however, the invention is not intended to be limited to these examples. Parts are by weight unless otherwise indicated.

#### EXAMPLE 1

##### A. Preparation of a Liquid Intermediate

A 1-liter stainless steel bomb was purged with nitrogen and charged with 284 grams (265 milliliters, 3.8 moles) of a 37% formalin solution (stabilized with 12% methanol). The bomb and contents were then cooled in a Dry Ice-acetone bath and the system evacuated. After hydrogen sulfide (225 grams, 6.75 moles) had been distilled into the bomb and liquefied therein, the bomb was sealed and heated at 60° C. for 4 hours. During this time the autogenous pressure was at least 25 atmospheres. The reaction vessel was then cooled to 0° C. and excess hydrogen sulfide was vented off to a caustic scrubbing tower. The 2-phase reaction mixture was poured into a separatory funnel. The lower layer which was collected, comprising the hydroxy mercapto liquid intermediate, weighed 210-230 grams (90-97% yield) and had a number-average molecular weight of 124-130. The procedure was repeated until a total of 1423 grams of product was made.

##### B. Conversion to the Mercapto-Terminated Polythiomethylene Compound

The intermediate prepared by the procedure of part A above (1423 grams) was heated, while rapidly stirred, at 100° C. for 6 hours in a reaction flask with concentrated hydrochloric acid (1000 milliliters) and boiled distilled water (2000 milliliters) under a nitrogen atmosphere. The resulting 2-phase reaction mixture was then cooled and filtered to remove some trithiane. The filtrate was transferred to a separatory funnel. The lower organic layer was separated, washed with two 500-milliliter portions of distilled water, and finally dried over anhydrous magnesium sulfate. The mercapto-terminated polythiomethylene compound obtained weighed 1090 grams (95% yield) and had a number-average molecular weight of 155.

C. When the procedure of part A above was repeated except that the reaction time was lengthened to 24 hours, a slightly lower yield (196 grams) of liquid intermediate resulted.

#### EXAMPLE 2

A nitrogen-purged 1-liter stainless steel shaker tube, charged with 37% formalin (284 grams, 265 milliliters, 3.8 moles formaldehyde) and hydrogen sulfide (225 grams, 6.75 moles) according to the procedure of Example 1, was agitated at 60° C. for a period of 4 hours.

After the shaker tube had been cooled to 0° C. and unreacted hydrogen sulfide had been vented off, it was opened and the contents removed. The pH of the aqueous phase was 3.5-4.0. The organic phase (the liquid intermediate) weighed 220 grams. A 15-gram sample of

the organic phase, dried over an anhydrous sodium sulfate, had a number-average molecular weight of about 152 and gave an infrared spectrum indicating the presence of HO-CH<sub>2</sub>- groups.

The aqueous phase (240 milliliters) was made 6 N in acid with concentrated sulfuric acid (40 milliliters). It was then combined with the remaining organic phase and agitated at 100° C. for 6 hours under a nitrogen atmosphere. The lower organic layer (200 grams) was separated, washed with water until the washings were neutral, and dried over anhydrous sodium sulfate. The organic polymer had a number-average molecular weight of about 152; its infrared spectrum indicated the absence of HO-CH<sub>2</sub>- groups.

#### EXAMPLE 3

Runs were made in which a 1-liter nitrogen-purged stainless steel bomb was charged according to the procedure of Example 1 with the following reactants:

Run No.	Molar Ratio, Hydrogen sulfide:Formaldehyde	Formaldehyde <sup>1</sup> weight (moles)	Hydrogen Sulfide weight
A-----	0.5:1	246 g. (3 moles)-----	51 g. (1.5 moles).
B-----	1:1	246 g. (3 moles)-----	102 g. (3 moles).
C-----	2:1	246 g. (3 moles)-----	204 g. (6 moles).
D-----	3:1	246 g. (3 moles)-----	306 g. (9 moles).
E-----	5:1	163 g. (2 moles)-----	240 g. (10 moles).
F-----	10:1	82 g. (1 mol)-----	340 g. (10 moles).
G-----	2:1	90 g. (3 moles)-----	204 g. (6 moles).

<sup>1</sup> 37% formalin solution (12% methanol stabilized) except for G where paraformaldehyde was used.

Each bomb was closed and rocked at 60° C. for 4 hours. The reaction mixtures were treated according to the procedure of Example 1A. The pH of the aqueous phases ranged between 3.4 and 4.2.

White, solid products containing both ether and thioether linkages were obtained from runs A and B. This result indicates that the desired liquid intermediates are not obtained when the hydrogen sulfide:formaldehyde molar ratio has a value of less than 1.75:1. Data for the remaining mixtures are shown in the table below.

Run No.	Number-average molecular weight of liquid intermediate	Yield of product based on formaldehyde charged, percent
C-----	122	98
D-----	108	99
E-----	100	99
F-----	95	97
G-----	124	74

#### EXAMPLE 4

A. Two 1-liter stainless steel bombs were charged according to the general procedure of Example 1 with 37% formalin (284 grams, 255 milliliters, 3.8 moles) and hydrogen sulfide (225 grams). Each bomb was then shaken for 4 hours at 60° C. The normally liquid intermediates were isolated by the procedure of Example 1A. The aqueous phases exhibited a pH of 3.5-4.0. The yield of intermediate in run A was 228.1 grams; run B gave 225 grams. 15-gram samples of the intermediates made in runs A and B were removed for analysis. The intermediates from runs A and B had number-average molecular weights of 122 and 124, respectively.

B. After concentrated hydrochloric acid (120 milliliters) had been added to the aqueous phase (220 milliliters) of run A to make it 6 normal in acid, it was combined with the organic phase and agitated at 100° C. for 6 hours under a nitrogen atmosphere. The layers were separated and the lower organic layer (205 grams) was washed with water until neutral and then dried over anhydrous sodium sulfate. A lesser amount of concentrated hydrochloric acid (20 milliliters) was added to the



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aqueous phase from run B to make it 0.1 normal in acid. The aqueous phase was then combined with the organic phase from run B and agitated at 100° C. for 6 hours under a nitrogen atmosphere. The organic phase, separated and purified by the procedure of A above, weighed 202.3 grams. The polymers from runs A and B, after the acid treatment, had number-average molecular weights of about 128 and 132, respectively.

#### EXAMPLE 5

##### *Increasing the Bis-Mercaptan Molecular Weight*

A 2-phase mixture of 155 grams of an HS-terminated polythiomethylene compound having a number-average molecular weight of 155 and 1000 grams of boiled distilled water was heated at reflux while rapidly stirred in a 3-liter flask. A nitrogen sweep, to expel the evolved hydrogen sulfide, was maintained throughout the reaction period. After the mixture had been heated under reflux for 8 hours, it was allowed to cool while stirred. The organic lower layer was separated, washed with water, and dried in a vacuum desiccator. The HS-terminated polythiomethylene compound thereby obtained weighed 143.2 grams and had a number-average molecular weight of 258 (boiling point elevation of acetone). Analysis: C, 22.9; H, 4.6; S, 68.4.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

What is claimed is:

1. A process for preparing mercapto-terminated thiomethylene compounds selected from the group consisting of methane dithiol and mercapto-terminated polythio-

6

methylenes which comprises (a) reacting 1.75 to 10 moles of hydrogen sulfide as a liquid with about one mol of formaldehyde at superatmospheric pressure and at temperatures between about 40° C. and 150° C. so as to produce a normally liquid intermediate whose infrared absorption spectrum indicates the presence of mercapto and hydroxyl groups; (b) contacting said intermediate with an aqueous non-oxidizing mineral acid at a temperature of about 25° C. to 175° C., at least until the infrared absorption characteristic of the hydroxyl group disappears; and (c) recovering the bis-mercaptan thereby formed which has the structure



15 where  $n$  is an integer of at least 1 indicating a number-average molecular weight up to about 160.

2. The process of claim 1 wherein the bis-mercaptan is contacted with water at about 100° C. whereby the number-average molecular weight is increased up to about

20 350.

3. The process of claim 1 wherein the non-oxidizing mineral acid is sulfuric acid.

4. The process of claim 1 wherein the non-oxidizing mineral acid is hydrochloric acid.

25 5. The process of claim 1 wherein the molar ratio of hydrogen sulfide to formaldehyde is about 2:1.

6. The process of claim 5 wherein the hydrogen sulfide is reacted with formaldehyde at a temperature of about 60° C.

30 7. The process of claim 6 wherein the intermediate is contacted with the aqueous non-oxidizing mineral acid at a temperature of about 100° C.

No references cited.

Appl. No. 09/992,054  
Response to Office Action  
Mailed March 21, 2008

## **APPENDIX B**

1

3,413,265

## HYDROLYTIC SCISSION OF POLYMERS CONTAINING GEM DITHIOETHER LINKAGES

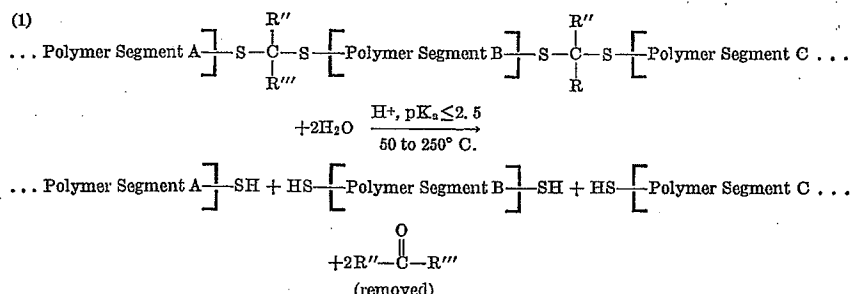
Eugene R. Bertozzi, Yardley, Pa., assignor to Thiokol Chemical Corporation, Bristol, Pa., a corporation of Delaware

No Drawing. Filed Aug. 31, 1965, Ser. No. 484,105  
12 Claims. (Cl. 260-46.5)

### ABSTRACT OF THE DISCLOSURE

A process is provided for preparing polymercaptan polymers by reacting polymers containing gem dithioether linkages with water in the presence of a strong nonoxidizing acid.

This invention relates to liquid or easily meltable polymercaptan containing polymeric products and to a process



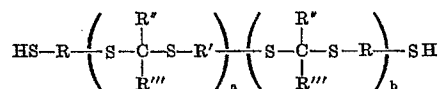
therefor. More particularly, this invention relates to polymercaptan containing polymers that are normally liquid at common room temperatures or are easily meltable solids and to a hydrolytic process for their formation.

It is an object of this invention to provide a novel method for preparing liquid or easily meltable polymeric materials which contain a plurality of mercaptan groups.

Another object is to provide novel curable liquid or easily meltable polymercaptan containing polymeric materials which subsequently may be oxidatively condensed or cured to form solid elastomers.

Yet other desirable objects will become evident from or are inherent in the following explanations, descriptions and examples.

Polymercaptan containing liquid or easily meltable polymers of this invention may be written

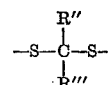


wherein R, R', R'' and R''' may be the same or different and are groupings that may be aliphatic, aromatic, alkaryl or siloxyl or mixtures thereof in nature the chains of which may occasionally be interrupted by chalcogen atoms, that is of oxygen and/or sulfur, by olefinic groups, viz  $\text{—CH=CH—}$ , or by urethane or polysulfide linkages;  $a$  is an integer from and including 0 to about 100 and  $b$  is an integer from 0 and including to about 100. R'' and R''' also may be hydrogen. By "easily meltable" is meant, for the purposes of this invention, a solid that melts to form a chemically stable liquid at or below  $100^\circ \text{C}$ . The polymeric products of this invention have molecular weights in the range of about 400 to 25,000.

The liquid or easily meltable polymers of this invention are formed by the hydrolytic scission of a carbonyl compound from solid and/or liquid polymer reactants of

2

from 5,000 to over 1,000,000 molecular weight which initially contain a plurality of gem dithioether groups. The gem dithioether group has the structure



wherein two thioether sulfur atoms are both bonded to the same carbon atom. This process, according to the invention, proceeds in the presence of water as a co-reactant and a catalytically effective quantity of a strong nonoxidizing acid, i.e. nonoxidizing acid with a  $\text{pK}_a$  not greater than about 2.5. It may be pictured as in Equation 1 for a reactant polymer having two gem dithioether linkages.

Thus, in order to obtain the instant polymercaptan containing polymers according to the invention, a polymer reactant must be used that contains a plurality, i.e. at least two, of gem dithioether linkages.

The extent to which the polymer reactant may be split into mercaptan-terminated molecules may generally be controlled, according to the invention, by controlling the amount of water reactant employed. In general, since each gem dithioether linkage requires a molecule of water to effect its splitting, therefore, under the conditions of the instant process complete scission of all gem dithioether linkages is possible in the presence of water molecules in amounts equal to or greater than the number of gem dithioether linkages present in the polymer reactant. Alternately, limited scission of the polymer reactant may be effected by using numbers of water molecules in amounts less than the number of gem dithioether groups originally present in the polymer reactant, i.e. water present in less than stoichiometric quantities. Hydrolytic splitting, in general, is effected in random fashion among the various gem dithioether linkages of the polymer reactant, thus when a less than stoichiometric amount of water is used, the specific gem dithioether groups undergoing splitting may be any of those present anywhere in the polymer molecular backbone. The mercaptan-terminated polymer molecules so produced, therefore, in gross view show a random distribution of molecular weights.

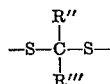
The average molecular weight of the mercaptan-terminated polymer molecules obtained may easily be prescribed according to the invention through a knowledge of the average number of gem dithioether linkages present per unit weight of the polymer, and through prescribing a quantity of water that is a specific fractional amount of the stoichiometric quantity of water needed to effect complete splitting. Thus, if there are an average of 10 gem dithioether linkages or 10 equivalent weights of gem dithioether linkages per arbitrarily chosen 10,000 molecular unit weight of a linear polymer reactant, then reaction of 10 molecules of water or 10 equivalent weights of water per unit weight of the poly-

mer reactant would, on the average, effect complete splitting and provide on the average dimercaptan-terminated polymer molecules with an average molecular weight of about 1,000. Reaction with 5 equivalents of water would provide on the average 5 mercaptan-terminated polymer molecules per 10,000 molecular unit weight of linear polymer reactant each with an average molecular weight of about 2,000, wherein each such dimercaptan molecule product on the average would still contain one equivalent weight of intact gem dithioether linkages. Conveniently, according to the invention, these calculations may be expressed by the several Formulae 2, 3 and 4.

The average molecular weight of polymercaptan polymer product obtained by complete hydrolytic splitting, i.e. when a stoichiometric amount of water is used which is to say when 1 mol of water per equivalent of gem dithioether linkage of the polymeric reactant is used, is provided by

$$(2) \quad \frac{W - A(CR''R''')}{A} = M$$

wherein A is the number of equivalents of gem dithioether linkages initially present per specific weight W, M is the average molecular weight of the polymercaptan polymer product, and  $(CR''R''')$  is the molecular weight of the group  $R''-C-R'''$  abstracted from the gem dithioether linkages,



when they are split. If the exact structure of the polymer reactant is unknown, which is commonly the case, the average molecular weight M of the polymercaptan polymer product may be simply determined by experiment, according to the invention. The purpose, first, is to find the number of gem dithioether linkages per unit weight W of polymer reactant. This is done by the hydrolytic splitting of all such linkages with water to provide mercaptan groups. The net number of equivalents of mercaptan groups so produced is twice the number of equivalents of gem dithioether linkages initially present in the polymer reactant. Thus, a known weight of poly(gem dithioether) containing polymer reactant initially is analyzed for number of mercaptan equivalents present per unit weight W of polymer reactant. A known weight of the polymer reactant is hydrolytically split using the instant process by increasing increments of water reactant until, by analysis, a constant number of mercaptan equivalents per unit weight W of polymer reactant is obtained with such increased incremental additions of water reactant. Then, simply, one half the net number of mercaptan equivalents per unit weight W of the polymer reactant equals A, the average number of gem dithioether linkages initially present per unit weight W. From A and W one may then calculate M by use of Equation 2.

The average molecular weight of dimercaptan polymer product obtained when less than the stoichiometric amount of water is used in hydrolytic splitting is provided by

$$(3) \quad \frac{W - B(CR''R''')}{B} = M$$

wherein W,  $CR''R'''$  and M are as was heretofore defined, and B is the number of mols or equivalent weights of water used per unit weight W, wherein  $B < A$ . Again M may be experimentally determined in identical manner as was described above, substituting B for A and wherein B is equal to the number of gem dithioether linkages split per unit weight of poly(gem dithioether) containing polymer reactant, or one-half the net number of mercaptan groups found after, and produced by, hydrolytic splitting. The specific dimercaptan product obtained by splitting a specific less than stoichiometric amount of gem dithioether linkages will thus contain on the aver-

age G number of gem dithioether linkages, which is the difference between the number of linkages split on complete hydrolytic splitting and the number split in the less than stoichiometric hydrolytic splitting. This is shown in Equation 4.

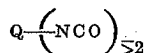
$$(4) \quad A - B = G$$

In Equations 2 and 3 the correction factors, viz.  $A(CR''R''')$  and  $B(CR''R''')$ , take into account the average loss of one carbon atom and  $R''$  and  $R'''$  group per dimercaptan product molecule formed. Although dimercaptan polymer products are obtained from linear poly(gem dithioether) containing polymer reactants, this invention also contemplates formation of tri- and higher polymercaptan products when branched poly(gem dithioether) polymer reactants are employed wherein each of the branches contains at least one gem dithioether linkage. For example a completely cured and crosslinked poly(gem dithioether) containing rubber or plastic may be hydrolytically split to branched polymercaptans by the instant process.

Polymeric reactants which are useful herein contain a plurality of gem dithioether linkages. They may be formed by sundry methods, such as by the inverse process of that shown in Equation 1, i.e. the joining of polymercaptans with carbonyl compounds and the formation and concomitant removal of water as a byproduct. Another useful method is to form specific poly(gem dithioether) polymethylene thioethers by the reaction of formaldehyde with hydrogen sulfide. Yet another and a preferred method to form useful poly(gem dithioether) polymer reactants is to react mercaptoalcohols with carbonyl compounds in the presence of non-oxidizing strong acid, and subsequently to polyetherify the gem dithioether diols obtained as reaction products by continually removing water produced as a byproduct in the presence of a strong nonoxidizing acid at an elevated temperature. In all of these methods it is possible to produce polymers of very high molecular weights such as crude rubbers or plastics say in the form of solid latex-like materials, or in the form of liquid polymers of lower molecular weights. In general, such polymeric substances formed by direct polymerization suffer from several disadvantages for use as, say, in situ moldable and curable polymers such as would be needed for sealant, potting and coating applications. The crude rubbers so prepared which are uncross-linked solids, would often require admixture with curing agents and adjuvants on a rubber mill prior to cure, and then subsequent vulcanization under pressure and at high temperatures. This forbids their "as is" use in in situ applications. The liquid poly(gem dithioether) containing polymer reactants prepared by direct polymerization often would not necessarily be curable per se, i.e. have no or insufficient reactive curing sites or reactive groups capable of ungoing curing reactions; or further such liquids often would be of such high viscosity as to forbid facile use even if they did contain sufficient curing sites. A further disadvantage to the direct end use of the polymer reactants stems from the fact that one may not easily prescribe their molecular weight merely by direct polymerization. It is now found, however, that it is a much simpler matter to selectively and prescribably split the high molecular weight polymer reactants to products of any desired and prescribable molecular weight by the teachings of this invention. The present process, indeed, provides a simple means to invariably provide curable polymers of unlimited storability and of a closely controlled average molecular weight that may be prescribed beforehand.

The preferred curable dimercaptan polymeric products of this invention are those prepared by the hydrolytic splitting of a poly(gem dithioether) polymer reactant formed first by the condensation of mercaptoalcohols with carbonyl compounds, and then by subsequent polyetherifica-

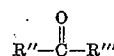
tion of the gem dithioether diol so produced; or, alternately, by reaction of the gem dithioether diol or its polyetherified product with a polyisocyanate which may be a simple compound or a urethane prepolymer to thus impart urethane properties when desired to the polymer backbone. Suitable polyisocyanates which may be used to provide such urethane linkages may be aliphatic or aromatic or alkaryl in nature. Typical of the useful simple polyisocyanates which may be used as is or to form prepolymers each of which may be reacted with gem dithioether containing substances to form the instant polymer reactants suitable for hydrolytic splitting are the aromatic diisocyanates, e.g. the isomers of toluene diisocyanate, m-phenylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 4,4'-biphenylene diisocyanate, and 1,5-naphthalene diisocyanate; and the aliphatic diisocyanates, such as 1,4-tetramethylene diisocyanate, 1,10-decamethylene diisocyanate, 1,4-cyclohexylene diisocyanate, and 4,4'-methylene-bis(cyclohexyl isocyanate); and the alkaryl diisocyanates, e.g. 4,4'-methylene-bis(phenylene isocyanate). They are used to join hydroxyl containing polymers which contain one or more gem dithioether linkages and thus provide suitable poly(gem dithioether) containing polymer reactants for present use which contain urethane linkages. The polymer reactants so formed should, however, contain no reactive isocyanate; this may easily be done by any of the sundry methods known to the art. In general, such useful urethane prepolymers are organic polymeric substances having a plurality of isocyanate groups, and are of the type depicted by the formula



The Q group is predominantly polymeric in nature. Prepolymers are usually formed from substantially linear polymers, i.e. with few if any branchings, that contain a plurality of active hydrogen atoms. The term "active hydrogen atom" refers to a hydrogen atom which displays activity according to the Zerewitinoff test as described by Kohler in J. Amer. Chem. Soc. 49, 3181 (1927). The polymeric portion may be polyester, polyether, polythioether, polyalkylene polysulfide and/or polysiloxane in nature. Suitable active hydrogen atom containing polymers useful to form the foregoing prepolymers include in their number such polyhydroxyl-containing polymers as polyhydroxy polyesters, and/or polyethers, and/or polythioethers, and/or polyalkylene polysulfides, and/or polysiloxanes. Suitable polyhydroxyl polyesters may be formed as the esterification products of polycarboxylic acids and polyols, using an excess of polyol. Suitable polyhydroxyl polyethers may be formed as the condensation products of polyols and polyepoxides with an excess of the former, or as the acid condensation products of polyols in a polyetherification reaction. Suitable polyhydroxyl polythioethers may be formed as the acid condensation products of such thiopolyols as thiodiglycol and/or another thioether diol. One may also use polyhydroxyl polyetherthioethers which may be formed as the condensation products of thioether diols and formaldehyde or a formaldehyde generating compound, or alternately by the acid condensation of a polyol ether and a polyol thioether, such as dihydroxy diethylene ether and thiodiglycol. Suitable polyhydroxyl polyalkylene polysulfide polymers may be prepared by any of the methods disclosed in U.S. Patents 2,527,375, 2,606,193, 2,676,165, and/or by the acid condensation polyetherification reaction of polyhydroxy alkylene polysulfides, such as the suitable polyhydroxy containing polysulfides disclosed in U.S. Patents 2,378,576, 2,484,369, 2,527,374, and 2,858,274, among others. Useful liquid polyhydroxyl polysiloxanes may be prepared by the conventional methods known in the art to prepare so called hydroxyl-end blocked polysiloxanes such as those liquids disclosed in U.S. Patents 2,843,555, 2,934,519, 3,019,204, 3,050,485, 3,050,491, 3,061,575, 3,070,566, 3,077,465, 3,109,826 and 3,110,689. Analogous

active hydrogen group containing polymers to the foregoing polyhydroxyl polymer, which have as their active hydrogen-containing groups either mercapto, primary and/or secondary amino, or carboxyl groups may also readily be prepared by methods well known in the art, and in turn also may be employed to prepare suitable prepolymers for present use.

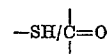
Typical of the poly(gem dithioether) polymers which may be used per se as a reactant herein, or may be combined with urethane prepolymers or simple polyisocyanates as described above to form reactants, are the hydroxyl-terminated polymers formed with alternating gem dithioether and ether linkages. A process for preparing these polymers is disclosed by E. R. Bertozzi et al. in the copending application entitled "Polymer Products and Process" Ser. No. 484,122, filed Aug. 31, 1965. To prepare these polymers one may proceed in a first step through the reaction of a mercaptoalcohol,  $HS-Q'-OH$ , with a carbonyl compound



such as an aldehyde or a ketone. The  $Q'$  group is an organic divalent intervening group that preferably may be non-reactive with isocyanate and is in general any organic group that is aliphatic, aromatic, alicyclic or alkaryl in nature and which indeed may contain pendant halogen, alkyl, nitro or other non-oxidizing chemical groups; the carbon chains thereof also may be interrupted by olefinic groups



or by chalcogen, that is sulfur and/or oxygen, atoms or by urethane or urea groups. The  $R''$  and  $R'''$  groups of the carbonyl are similarly defined as is  $Q'$ , but are monovalent in nature and additionally may be hydrogen, as in formaldehyde. Further  $R''$  and  $R'''$  may be the same or different. According to this technique the reactants mercaptoalcohol and carbonyl, first are admixed in the presence of a strong nonoxidizing acid, which acts as a catalyst, and in the absence of water. An inert organic solvent is usually present as a process acid. At this point, mercaptan groups of the alcohol preferentially react with the carbonyl with the evolution of heat to form a dihydroxy gem dithioether, wherein the terminal hydroxyl are each separated from the central gem dithioether group by the intervening group  $Q'$ . Water is produced as a by-product. This reaction is continued until substantially all mercaptan groups have reacted with carbonyl, e.g. two equivalents of mercaptan per equivalent of carbonyl to provide each equivalent of gem dithioether and mol of water. It is desirable that the ratio of equivalents of mercaptan to carbonyl,



not be less than 2/1, so to substantially avoid the formation of gem diether linkages, which deleteriously would form hydroxyl terminals rather than mercaptan terminals in the instant hydrolytic splitting process. Thus by prescribing an



ratio of 2/1 only the dihydroxy gem dithioether compound is formed. The formation of the dihydroxy gem dithioether may be conducted at effective temperatures of 15 to 150° C. in effective reaction intervals of about 0.5 to 60 minutes. One then may prepare suitable polymer reactants for this invention which contain sequentially alternate linkages of gem dithioether and ether groups by etherification of the dihydroxy gem dithioether compound are joined in chain-extension with ether linkages by forcible removal both of the water of reaction formed in the

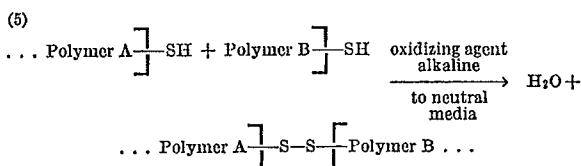
condensation of carbonyl and mercaptoalcohol and the water formed by etherification of the terminal hydroxyls of the dihydroxy gem dithioether at elevated temperatures and in the presence of catalytically effective quantities of a strong non-oxidizing acid.

Hydrolytic splitting of poly(gem dithioether) containing polymer reactants as exemplarily shown in Equation 1, according to the present invention, is carried out in the presence of catalytically effective quantities of a strong non-oxidizing acid, i.e., one with a  $pK_a$  of 2.5 or less. Both inorganic and organic acids are usefully employed singly or in combination, and include in their number such inorganic acids as sulfuric, hydrochloric, phosphoric, phosphorous and pyrophosphoric acids and such organic acids as dichloroacetic, glycerophosphoric, maleic, oxalic, trichloroacetic and p-toluene sulfonic acids. Catalytically effective amounts may be as little as 0.005 equivalent to as much as five acid equivalents of acid per equivalent or mol of water reactant.

Hydrolytic splitting, according to the invention, is carried out at elevated temperatures, i.e. above common room temperatures, and preferably within the range of about 50 to 250° C. Advantageously it is carried out until, for any amount of water charged, the mercaptan content of the product has become substantially constant with reaction time. This may occur in from as little as 30 minutes to as many as 200 hours, depending upon the amount of catalyst present and the temperature of reaction employed. Conveniently the polymer reactant may be charged to the reaction vessel in bulk, and if solid in a particulate form. Alternately, the polymer reactant may be charged as a solution of a solid dispersion in an inert organic solvent, such as an aliphatic or aromatic hydrocarbon or oxyhydrocarbon. The water reactant is then charged either all at one time, in discrete incremental quantities or continuously during the course of the hydrolytic reaction. The pot mixture of reactants is elevated to reaction temperatures either prior to or subsequent to the charge of a catalytically effective quantity of a non-oxidizing strong acid. An exemplary temperature therefor is 90° C. The reaction mixture is usually agitated during the course of reaction to promote better contact between the reactants. At intervals throughout, small quantities of the pot mixture may be removed to determine mercaptan content. The carbonyl byproduct evolved may be cautiously removed without removing water reactant during the course of reaction, thus promoting further hydrolytic splitting and a complete utilization of the water reactant. This may also be done, depending upon the physical or chemical nature of the carbonyl byproduct by such diverse means as complex formation of carbonyl and removal of the complex, as one may with acetaldehyde or formaldehyde and sodium bisulfite, or by a volatilization of the carbonyl and yet not the water, as one indeed may when acetone is formed as the byproduct of the hydrolytic splitting, and so forth. Alternately one may practice the instant process by only slowly charging the water either incrementally or continuously and removing the carbonyl formed immediately upon its formation thus driving reaction 1 to completion. Further, one may charge water in such small quantities that all will react completely due to the many gem dithioether linkages present by virtue of the Law of Mass Action. One may also charge more than a stoichiometric amount of water reactant to effect a complete hydrolytic split of all gem dithioether linkages in the high molecular weight polymer reactant, and then at some desired viscosity of liquid polymer product or at any desired mercaptan content of the product stop the splitting process by neutralizing the acid catalyst. At any event, regardless of the specific mode and exact technique that may be chosen to practice the instant process, it thus provides a controllable means by which one may theoretically specify beforehand and, in practice, provide curable polymercaptan polymers of any prescribed and desired average molecular weight, of any

desired and prescribable molecular backbone configuration and of any desired and prescribable chemical and physical properties.

The polymercaptans of this invention are curable, that is to say they may be consecutively chain extended or conjoined to form molecules of increased molecular weight. For example, they may be oxidatively cured, to form larger molecules conjoined by disulfide linkages, and to form water as the byproduct such as is pictured in Equation 5.

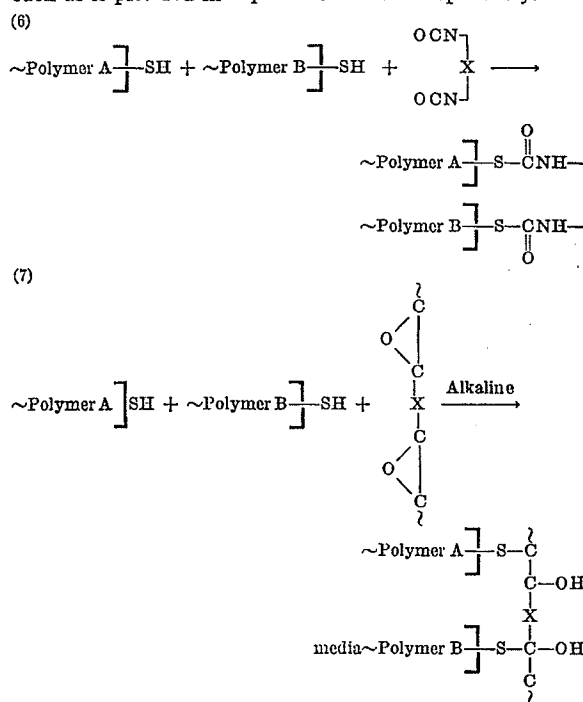


Exemplary oxidizing curing agents which may be used are listed in Table II.

TABLE II.—OXIDIZING CURING AGENTS

Inorganic oxides		Inorganic peroxides		Inorganic oxidizing agents	
ZnO	FEO	ZnO <sub>2</sub>	FeO <sub>2</sub>	Na <sub>2</sub> CrO <sub>4</sub>	NaClO <sub>4</sub>
PbO	Fe <sub>2</sub> O <sub>3</sub>	PbO <sub>2</sub>	As <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> CrO <sub>4</sub>	KClO <sub>4</sub>
MgO	CoO	MgO <sub>2</sub>	Sb <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Ba(ClO <sub>4</sub> ) <sub>2</sub>
CaO	CuO	CaO <sub>2</sub>	Sb <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>
BaO		MnO <sub>2</sub>	SnO <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> NO <sub>3</sub>
		TeO <sub>2</sub>	Pb <sub>2</sub> O <sub>4</sub>		
		SeO <sub>2</sub>			
Organic peroxides				Organic oxidizing agents	
Benzoyl peroxide.				Nitrobenzene.	
Dicumyl peroxide.				Dinitrobenzene.	
Cumene hydroperoxide.				Trinitrobenzene.	
t-Butyl hydroperoxide.				Trinitrotoluene.	
t-Butyl perbenzoate.				Other nitro compounds.	
				p-Quinone dioxime.	
				Other oximes.	

Alternately, they may be cured by condensation reactions with polyisocyanates to form polythiourethane linked polymers of higher molecular weight, or with polyepoxides to form polythioether linked polymers with pendant hydroxyl groups and higher molecular weight, such as is pictured in Equations 6 and 7 respectively.

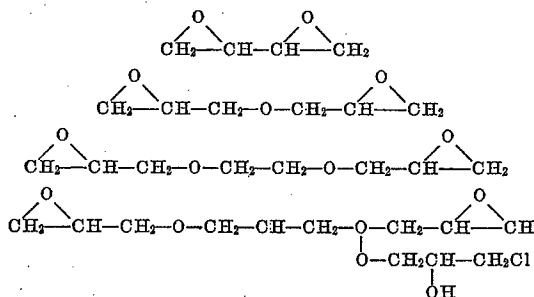


Therein X is a divalent intervening group defined as is R above.

The polyepoxide curing agents which also may be used to cure the instant polymercaptan polymers are those materials which have an average oxirane functionality of

approximately two or more, that is, they are materials which contain an average of at least approximately two epoxide groups per molecule of the polyepoxide material. The position of the epoxide groups in the polyepoxide curing agent is not critical. For instance, if the polyepoxy material is essentially linear in structure the epoxide groups may be in a terminal position or they may be positioned intermediately and/or randomly along the linear structure. Polyepoxide materials which may be used as curing agents herein include the following types of materials.

(1) Essentially linear type such as



and the epoxidized polybutadiene materials such as those which have an epoxide functionality of four or more and are sold commercially under the designation "Oxiron" resins, i.e., "Oxiron 2001" and "Oxiron 2002."

(2) Bisphenol A/epichlorohydrin reaction products which are aromatic in nature and which include those sold commercially under the trademark designations "Tipox," i.e., "Tipox A," "Tipox B" and "Tipox C" resins; "Epon," i.e., "Epon 828" resin; and "Bakelite," i.e., "Bakelite ERL" resin. (Bisphenol A, chemically, is p,p'-isopropylidenediphenol.)

(3) Cyclo-aliphatic type which includes those sold commercially under the designation "Unox" resins, i.e., "Unox 206" which is epoxy ethyl-3,4-epoxy cyclohexane and "Unox 201" which is 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate.

(4) Resorcinol diglycidyl ether type which includes those sold commercially under the designation "Kopoxite" resins, i.e., "Kopoxite 159."

(5) Epoxy novolak type alkyl novolak resins which are phenolic/epoxy type systems and which include the resin sold commercially under the designation "Dow Epoxy Novolak 438" or "DEN 438-EK 85" which contains 85% resin by weight and 15% methyl ethyl ketone as a solvent therefor, and the resins sold commercially under the designation "KER" resins, i.e., "KER 357A" and "KER 955A."

(6) Epoxidized fatty acid resins including those which are sold commercially under the designation "Epoxol" such as "Epoxol 9-5."

The polymercaptan polymers of the present invention have unique utility in that they have indefinite storage life and they are oxidatively or otherwise curable to form useful solids, such as elastomers or plastics. Cure of the instant polymer disulfide linkages formation especially desirable from the point of providing the cured products with an enhanced resistance to dissolution and/or chemical attack.

In order to cure the present polymercaptan containing polymers, they are uniformly admixed with the curing agent in such relative quantities as will provide a suitable number of mercaptan equivalents of polymer, usually one, per equivalent of curing agent to effect cure; the latter is based usually upon its oxidizing ability that is to say the number of and oxidizing effectiveness of the oxidizing groups or the number of isocyanate or oxirane groups available per molecule of curing agent. Usually stoichiometric quantities of equivalents of mercaptan and curing agent will provide adequate cures. With some agents such as PbO<sub>2</sub> or polyepoxides curing may be carried out at

common room temperatures or above, whereas with others, such as cumene hydroperoxide or ZnO<sub>2</sub> elevated temperatures are needed to promote cure. The cure products obtained are usually solid materials, that may be formed, according to the specific chemical nature of the specific reactants and their polymeric backbone, into chemically or abrasion resistant puttylike materials or castings, films, plastics, elastomers, sealants, threads, coatings and the like. Liquid cure products also may be formed which may be used as inert lubricants.

The following examples illustrate modes of practice of the present invention but are not intended to limit the scope thereof.

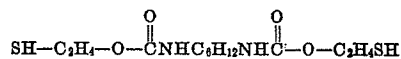
#### EXAMPLE 1

##### A. Preparation of a poly(gem dithioether) containing polyurethane reactant

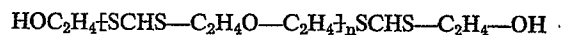
About 2 mols (156 g.) of 2-mercaptoethanol and 1 mol (44 g.) of acetaldehyde were reacted for about 10 hours at 50° C. in the presence of 0.2 ml. of concentrated sulfuric acid catalyst to provide the dihydroxy diethylene (methyl gem dithioether). About 70 ml. of benzene was added. In etherification the water of reaction was then forcibly removed by azeotropic distillation, the pot contents were neutralized at room temperature with CaO, and volatiles were removed by distillation. The pot product upon cooling formed a wax-like solid polymer in 120 g. yield, or 73.2% of theoretical. The polymer obtained had a melting point of about 88° C., 40.9 wt. percent sulfur, 5.62 wt. percent hydroxyl, by analysis and a molecular weight of about 605, based on the hydroxyl content. A polyurethane rubber is formed from the poly[ethylene (methyl gem dithioether) (ether)] diol prepared as above by reaction with hexamethylene diisocyanate in such quantities as to provide a ratio of equivalents of isocyanate to equivalents of hydroxyl of 1/1 in an environment otherwise free of active hydrogen-containing materials, under dry nitrogen gas, upon admixture at 120° C., for about 2 hours.

##### B. Preparation of a polymercaptan-polyurethane polymer of the invention

The poly(gem dithioether)-containing polyurethane rubber, prepared as in A above is abraded and cut to form a powdery material of small particle size. The mercaptan content of the reactant is obtained by analysis. Approximately 60 g. of the particulate rubber is suspended and dispersed in about 150 ml. of dry benzene in an enclosed reflux reaction vessel. To this is added 0.5 ml. of concentrated sulfuric acid. The temperature of the suspension is raised to about 80° C., the reflux temperature of benzene, and is maintained thereat. Water in 1 gram increments is charged thereto at intervals of about 0.5 hour each. This is continued until the mercaptan content of the pot product remains constant with incremental additions of water. At this point complete hydrolytic scission of all gem dithioether linkages to mercaptan terminals is achieved and all particles of rubber reactant have disappeared. Solvent and acetaldehyde produced as the by-product are removed from the pot product mixture by volatilization at about 40° C. and at about 20 mm. of Hg. The dimercaptan product remaining is a liquid mixture of the ether dimercaptan HS—C<sub>2</sub>H<sub>4</sub>—O—C<sub>2</sub>H<sub>4</sub>—SH of molecular weight 138 and the diurethane dimercaptan



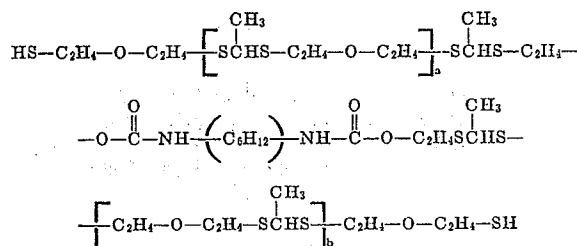
of molecular weight 324 in the number proportions of about 4/1 to 5/1. This is determined by analysis. This also is easily calculated from the stoichiometry of the reactions in that each two polymeric wax molecules of about 605 molecular weight are conjoined by one hexamethylene diisocyanate molecule, and that each wax molecule by its mode of formation has a structure



Each wax molecule therefore has about 4 to 5 equivalents of gem dithioether linkages, one of which, on the average, will constitute terminals for the diurethane dimercaptan, and the others for the ether dimercaptan when hydrolytic scission is complete.

In similar fashion to that used above to provide complete hydrolytic scission of the polyurethane poly(gem dithioether) polyether rubber to a mixture of substantially non-polymeric dimercaptans, partial hydrolytic splitting to form easily meltable polymeric polyurethane dimercaptans is here achieved by reaction of the rubber with a less than stoichiometric quantity of water required for complete scission.

An easily meltable mercaptan-containing poly[ethylene diurethane (gem dithioether) (ether)] polymer of this invention is prepared substantially according to the method as was described above for complete scission, using 0.01 mol or 0.18 g. of water with approximately 6 g. of powdered rubber, prepared as in A, until the mercaptan content is constant. Since there are between 4 to 5 equivalents of gem dithioether linkages per 600 molecular weight unit of the rubber reactant, as was determined by the mercaptan content obtained upon complete hydrolysis, one mol of water per 600 g. of rubber would split the rubber on the average into dimercapto-diurethane ether polymer molecules of about 600 molecular weight and containing approximately 3 to 4 unsplit gem dithioether linkages per molecule. An easily meltable polymer conforming to the structure



of approximately 600 to 700 molecular weight is obtained by this incomplete hydrolytic scission, wherein  $a+b$  is from 1 to 2.

#### C. Cure of polymercaptan-polyurethane polymer of the invention

(1) One hundredth mol, about 6 g., of the dimercaptan liquid polymer product formed as in B above is uniformly admixed with about 6 g. of a liquid polymeric diepoxide formed as the reaction product of epichlorohydrin and *p,p'*-isopropylidenediphenol having an epoxide equivalent of about 225 and a viscosity of about 300 poises at 25° C. To this is added 0.1 g. of the catalyst 2,4,6-tri(dimethylaminomethyl)phenol. The admixture is poured into a mold and permitted to stand at about 80° C. and within 10 hours a clear flexibilized plastic object is formed which has the configuration of the mold.

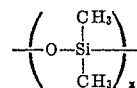
(2) One hundredth mol, 6 g., of the dimercaptan polymer product formed as in B above is uniformly admixed with 1 g. of tellurium dioxide,  $\text{TeO}_2$ . The admixture at 90° C. quickly solidifies to form an elastomeric polysulfide rubber product with properties suitable for use in cast printing roll applications.

(3) One hundredth mol, 6 g., of the dimercaptan polymer product formed as in B above is uniformly admixed with 2,4-toluene diisocyanate in such quantities so as to provide a ratio of equivalents of isocyanate to equivalents of mercaptan, NCO/SH, of 2/1 in an inert environment. A diisocyanate functional urethane prepolymer is obtained, which upon admixture with water in the presence of a base forms a plastic-like foam, and upon admixture with a dihydroxyl functional polyether glycol of about 2,000 molecular weight forms a urethane elastomer. When the dimercaptan is admixed with 2,4-toluene diisocyanate

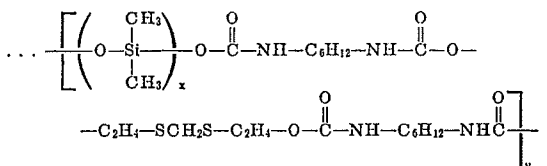
in a ratio NCO/SH of 1/1, a useful thiourethane elastomer is obtained.

#### EXAMPLE 2

A solid copolymer containing 400 molecular weight units of dimethyl polysiloxane,

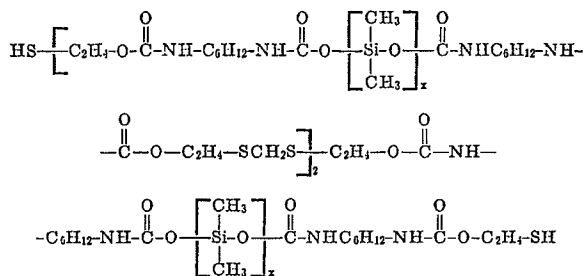


conjoined to diethylene gem dithioether groupings by hexamethylene diurethane bridges which substantially has the unit formula



with one gem dithioether linkage per unit molecular weight, e.g. that which is between the formula brackets, of about 922, is hydrolytically split to a dimercaptan poly (polydimethyl siloxyl diethylene gem dithioether) liquid polymer of this invention having an average molecular weight of about 2,700 by admixture of a benzene suspension of about 92.2 g. of the powdered copolymer which contains about 0.1 g. equivalent of gem dithioether linkage, in 200 ml. of benzene with 0.6 g. or about 0.033 g. equivalent of water in an inert environment and in the presence of 0.03 g. equivalent of *p*-toluene sulfonic acid. The temperature is elevated to the reflux temperature of the solvent and maintained therewith with mixing of the reactants until the mercaptan content becomes constant with time.

The liquid dimercaptan product obtained is separated from the solvent and formaldehyde formed as the by-product by volatilization; the product has the structure



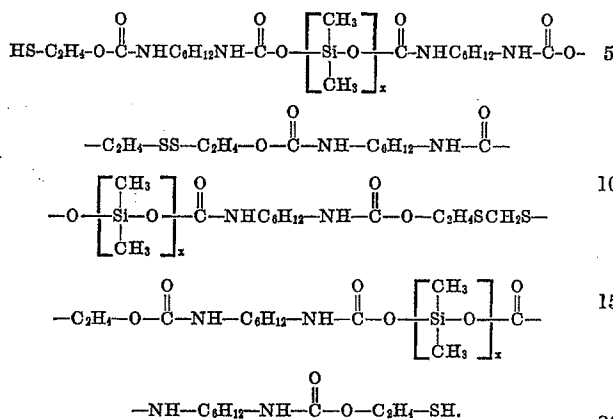
and has on the average a molecular weight of approximately 2,700. It is curable with oxidizing agents to provide disulfide linked elastomers, with polyepoxides to provide useful abrasion resistant flexible plastics and with polyisocyanates to provide foams, rubbers or plastics.

#### EXAMPLE 3

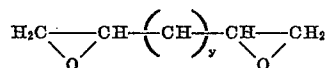
The liquid dimercaptan poly[poly(dimethyl siloxyl)diethylene (gem dithioether)] polymer of about 2,700 molecular weight and formed as in Example 2 is cured to a disulfide linked rubber with lead dioxide,  $\text{PbO}_2$ , at 80° F. in a period of about 24 hours. The rubber is then comminuted, and about 27 g. of the rubber powder is suspended in 100 ml. of the inert liquid dioxane, 1,4-diethylene dioxide. To this is charged about 0.3 ml. of pyrophosphoric acid. The temperature of the pot mixture is elevated to reflux, about 100–105° C.; about 0.18 g. of water is charged thereto. Reflux is maintained until the mercaptan content remains constant with time. The solvent and formaldehyde produced as a byproduct are separated from the liquid disulfide-containing polymer product. The polymer



product also has a molecular weight of about 2,700, and has a structure which corresponds to



The foregoing liquid disulfide-containing polymer product is cured to a solid plastic by reaction in an alkaline medium of 1 mol with 1 mol of a liquid polyalkylene diepoxide of the formula



and having a molecular weight of 1,300. The plastic is comminuted and 40 g. of the powdered plastic is suspended in 100 ml. of toluene. To this is charged about 0.5 ml. of trichloroacetic acid. The temperature of the pot contents is raised to permit the toluene to reflux at about 110 to 115° C. About 0.18 g. of water is charged thereto, and heating is continued until the mercaptan content of the pot contents remains constant with heating time. The solvent and formaldehyde produced as the reaction byproduct are removed by volatilization at lower than atmospheric pressures and at about 50° C. The product obtained is a curable dimercaptan-containing liquid polymer, that on the average no longer contains any gem dithioether linkages, but does contain two pendant hydroxyl groups, two terminal mercaptan groups, three 400 molecular weight blocks of poly(dimethylsiloxyl) groups, six hexamethylene diurethane groups, one disulfide linkage, two thioether linkages, and one polymethylene group of about 1,300 molecular weight which contains at its ends the hydroxyl groups, all joined one to another with ethylene groups.

The foregoing dimercaptan polymer is cured by oxidizing agents to provide disulfide linked rubbers containing no gem dithioether groups, by polyepoxides to form hydroxyl-containing plastics containing thioether but no gem dithioether linkages, and by polyisocyanates to form thiourethane-containing foams, rubbers and plastics which contain no gem dithioether linkages.

The foregoing examples illustrate how by the method of this invention it is possible to sequentially hydrolyze a poly(gem dithioether) containing polymer, to lower molecular weight polymercaptan polymers then cure the polymercaptan polymeric product of hydrolysis in such a way as to join together blocks of polymeric units of diverse nature, e.g. join say a polysiloxane backbone, to a polyethylene backbone, or to a polyurethane backbone, all at will and to form prescribable products, by newly formed

linkages that also are prescribable and may be thioether or thiourethane or disulfide in nature.

I claim:

1. A method for preparing a polymeric polymercaptan which comprises reacting, at a temperature above common room temperature a carbonyl polymeric reactant material of from 5,000 to over 1,000,000 molecular weight containing a plurality of gem dithioether linkages with water in the presence of a catalytically effective amount of a strong nonoxidizing acid to cleave hydrolytically the gem dithioether linkages, separating and recovering the resulting polymeric polymercaptan product of the hydrolytic scission therefrom.

2. A method as in claim 1 wherein said strong non-oxidizing acid has a  $\text{pK}_a$  value of at most 2.5.

3. A method as in claim 2 wherein said acid is selected from the class consisting of sulfuric, hydrochloric, phosphoric, phosphorous, pyrophosphoric, dichloroacetic, glycerophosphoric, maleic, oxalic, trichloroacetic and p-toluene sulfonic acids.

4. A method as in claim 1 wherein said acid is present in quantities of from 0.005 to 5 acid equivalents per mol of water reactant present.

5. A method as in claim 1 wherein the ratio of the number of equivalents of gem dithioether linkages per unit weight of said polymeric material present to the number of mols of water reactant hydrolytically cleaving per unit weight of said polymeric material present is  $\leq 1/1$ .

6. A method as in claim 1 wherein the ratio of the number of equivalents of gem dithioether linkages per unit weight of said polymeric material to the number of mols of water reactant hydrolytically cleaving per unit weight of said polymeric material is  $> 1/1$ .

7. A method as in claim 1 wherein said hydrolytically cleaving is conducted at a temperature in the range of about 50 to 250° C.

8. A method as in claim 1 wherein said polymeric reactant material additionally contains a plurality of linkages selected from the class consisting of thiourethane, urethane, ether, thioether, polysulfide and siloxyl linkages.

9. A method as in claim 1 wherein said polymeric polymercaptan product is a liquid.

10. A method as in claim 1 wherein said polymeric polymercaptan product is a solid.

11. A method as in claim 1 wherein said polymeric polymercaptan product contains a plurality of linkages selected from the class consisting of thiourethane, urethane, ether, thioether, gem dithioether, polysulfide and siloxyl linkages.

12. A method as in claim 1 wherein said hydrolytically cleaving is conducted in the presence of an inert organic solvent.

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2,466,963	4/1949	Patrick et al	260—79.1
3,016,365	1/1962	Holtschmidt	260—79
3,314,913	4/1967	Deutschman et al.	260—79
3,317,461	5/1967	Plueddemann	260—79

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M. I. MARQUIS, *Assistant Examiner.*

Appl. No. 09/992,054  
Response to Office Action  
Mailed March 21, 2008

## **APPENDIX C**

**United States Patent** [19]

Deisenroth et al.

[11] **Patent Number:** 5,708,119[45] **Date of Patent:** Jan. 13, 1998[54] **PERFLUOROALKYL SULFIDE, SULFONE,  
POLYSULFONE AND POLYSULFIDE DIOLS**[75] **Inventors:** Ted Deisenroth, Carmel, N.Y.; Marlon  
Haniff, West Orange, N.J.[73] **Assignee:** Ciba Specialty Chemicals  
Corporation, Tarrytown, N.Y.[21] **Appl. No.:** 665,125[22] **Filed:** Jun. 14, 1996**Related U.S. Application Data**[62] **Division of Ser. No. 270,067, Jul. 1, 1994, abandoned.**[51] **Int. Cl.<sup>6</sup>** ..... C08G 18/28; C08G 18/70[52] **U.S. Cl.** ..... 528/70; 528/44; 528/65;  
528/87; 528/321; 528/401; 528/422; 528/495;  
528/499; 528/503; 560/227[58] **Field of Search** ..... 528/44, 65, 70,  
528/87, 321, 401, 432, 495, 499, 503; 560/227[56] **References Cited****U.S. PATENT DOCUMENTS**

4,946,992 8/1990 Falk et al. .... 560/227

**OTHER PUBLICATIONS**

Journal of Fluorine Chemistry 51(1991) 43-52 "Synthetic  
Utility of 3-(Perfluoro-1,1-dimethylbutyl) 1-propene"  
Halina Plen Kiewicz et al.

*Primary Examiner*—James J. Seidleck*Assistant Examiner*—Duc Truong*Attorney, Agent, or Firm*—Kevin T. Mansfield[57] **ABSTRACT**

Bisperfluoroalkyl-substituted diols containing sulfide, sulfone or polysulfide linkages and a method for making them are described. These diols can react with isocyanates to form urethanes; diisocyanates to form polyurethanes; chloroformates to form carbonates; with carboxylic, sulfuric or phosphoric acids or derivatives to form carboxylate esters, sulfate esters, phosphate esters respectively. These diol compounds and their derivatives are useful for imparting oil and water repellency to substrates such as glass, wood, paper, leather, wool, cotton, polyester and other substrates.

**4 Claims, No Drawings**

# PERFLUOROALKYL SULFIDE, SULFONE, POLYSULFONE AND POLYSULFIDE DIOLS

This application is a Division of Ser. No. 08/270,067 filed Jul. 5, 1994 now abandoned.

## BACKGROUND OF THE INVENTION

This invention relates to bisperfluoroalkyldiols and their derivatives which impart oil water repellency on materials such as glass, wood, paper, leather, wool, cotton, polyester and other substrates.

Perfluoroalkyl-substituted polymers possess free surface energies even lower than that of poly-tetrafluoroethylene (Teflon). They have therefore long been used to impart oil- and water repellency to a wide variety of substrates, especially textiles. Phosphate esters of perfluoroalkyl-substituted alcohols are also being used as oil- and water repellent paper sizes, for instance in paper plates and in food packaging products. In these applications it is especially important that the paper sizing compound contain at least two perfluoroalkyl or  $R_F$  groups. When mono- $R_F$  alcohols are used to esterify phosphoric acid, only the diesters are active oil- and water repellents. The monoester is too water soluble and, even if retained on the cellulose fiber, reduces water repellency, and the triester is not substantive. However making phosphate diesters in high yield is very difficult in practice; substantial amounts of mono- and triesters are always produced as by products. It is also impossible to prepare oil- and water-repellent paper sizes in form of sulfuric acid half-esters from mono- $R_F$  alcohols, since such esters are very water soluble anionic surfactants and have a detrimental effect on water repellency. Mono- $R_F$ -substituted alcohols and diols, though suitable for the preparation of acrylic and methacrylic oil- and water-repellent  $R_F$ -polymers, are therefore less suitable for the preparation of oil-repellent phosphate or sulfate ester acidic paper sizes.

The use of di- $R_F$ -substituted alcohols and diols makes it possible to prepare highly oil-repellent phosphate or sulfate monoester paper sizes, since even a mono-ester contains two  $R_F$  groups. This approach and some such compounds are described in U.S. Pat. Nos. 5,091,550 and 5,132,445.

For the preparation of oil- and water-repellent polyurethanes it is especially important that the diol contain more than one  $R_F$  group. Cemin such diols and polyurethanes thereof are described in U.S. Pat. Nos. 3,935,277; 3,968,066; 4,046,944; 4,054,592; 4,098,742; 4,946,992 and 5,200,493.

Although the di- $R_F$ -substituted phosphates and  $R_F$ -substituted polyurethanes described in the above patents show excellent performance, the synthesis of the bisperfluoroalkyl-substituted diols involve many steps and costly intermediates such as  $R_F$ -ethylenethiols and halogenated alcohols and diols. Copending application Ser. No. 08/420,386, now U.S. Pat. No. 5,585,517 describes bisperfluoroalkyl-substituted diols produced by a more straightforward synthesis route, namely by direct addition of perfluoroalkyl iodides ( $R_F$ -I) to diallyl diols, followed by elimination of HI with a base. Another synthetic route to di- $R_F$ -diols is described in J. Fluorine Chemistry, 62, (1993), p. 161-171. It involves the dimerization of  $R_F$ -allyl acetate adducts with zinc. The yields are less than 60% and numerous by-products are formed.

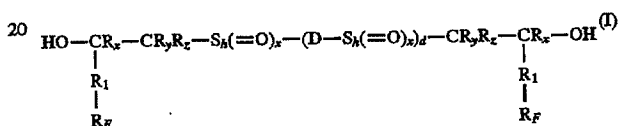
It has now been discovered that bisperfluoroalkyl-substituted diols can be synthesized in high yield and purity by reaction of an  $R_F$ -substituted epoxide with sulfide ions in the presence of a base. These novel diols, containing sulfide, polysulfide, sulfone, polysulfone and di-thioether moieties,

have not been previously reported. They are useful for synthesizing perfluoroalkyl-substituted urethanes, polyurethanes, carboxylate esters and acids, polyesters, sulfate esters and acids, phosphate esters and acids, and carbonate esters and acids. These compounds are isolated in high yield and purity.

Some dicarboxylic acids, their metal salts and lower alkyl esters which contain two polyfluoroalkoxyalkyl carboxy moieties joined by —S— or a —S—alkylene—S— crosslink have been reported in U.S. Pat. No. 3,828,098. Also, certain structures of the type  $R_F-S_x-R'_F$  have been reported in U.S. Pat. No. 3,700,646, where  $R_F$  and  $R'_F$  are polyfluoroalkoxyalkyl radicals and x is 1 to 8. Such materials would be difficult to derivatize without significant functional group transformations.

## DETAILED DISCLOSURE

The new bisperfluoroalkyldiols are of the formula I



wherein

$R_1$  is a direct bond, a branched or linear alkylene of up to 6 carbon atoms, alkyleneoxyalkylene of up to 6 carbon atoms, alkyleneethioalkylene of up to 6 carbon atoms, alkyleneoxy of up to 6 carbon atoms, alkenyleneoxyalkylene of up to 6 carbon atoms, alkyleneethioalkyleneoxyalkylene of up to 9 carbon atoms, carbonamidoalkylene where the alkylene moiety contains up to 6 carbon atoms and the amido nitrogen is unsubstituted or further substituted by lower alkyl, sulfonamidoalkylene wherein the alkylene moiety contains up to 6 carbon atoms and the amido nitrogen is unsubstituted or further substituted by lower alkyl; carbonamidoalkyleneethioalkylene wherein the carbonamidoalkylene moiety is as defined hereinabove and the thioalkylene moiety contains up to 6 carbon atoms, or sulfonamidoalkyleneethioalkylene wherein the sulfonamidoalkylene moiety is as defined hereinabove and the thioalkylene moiety contains up to 6 carbon atoms,  $R_x$ ,  $R_y$  and  $R_z$  are independently of each other alkyl groups with 1-5 carbon atoms or hydrogen,

h is 1 or 2,  
x is 0, 1, or 2, with the proviso that when h is 2, x is 0,  
d is 0 or 1,

D is an alkylene group with 2 to 10 carbon atoms, a dialkylene ether group with 4 to 10 carbon atoms, or pentaerythritol diacetate or dipropionate, and

$R_F$  is a monovalent, perfluorinated, alkyl or alkenyl, straight, branched or cyclic, organic radical having 3 to 20 fully fluorinated carbon atoms, which radical can be interrupted by one or more divalent oxygen or sulfur atoms, and each  $R_F$  radical is the same or different.

By lower alkyl is meant  $C_1$ - $C_5$ alkyl.

Preferred are compounds wherein  $R_x$  is a direct bond, —CH<sub>2</sub>—, —CH<sub>2</sub>CH<sub>2</sub>—O—CH<sub>2</sub>—, —CH(CH<sub>3</sub>)—, —CH<sub>2</sub>CH<sub>2</sub>—S—CH<sub>2</sub>—, —CH=CHCH<sub>2</sub>—O—CH<sub>2</sub>—, —SO<sub>2</sub>NR<sub>2</sub>—CH<sub>2</sub>— or —CONH—CH<sub>2</sub>CH<sub>2</sub>—O—CH<sub>2</sub>—, wherein  $R_2$  is hydrogen or an alkyl group with 1 to 4 carbon atoms,  $R_x$  is methyl or hydrogen,  $R_y$  and  $R_z$  are hydrogen, h is 1, x and d are zero and the  $R_F$  group is saturated, contains 6-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group.

Also preferred are compounds wherein  $R_1$  is a direct bond, —CH<sub>2</sub>—, —CH<sub>2</sub>CH<sub>2</sub>—O—CH<sub>2</sub>—, —CH<sub>2</sub>CH<sub>2</sub>—

$S-CH_2-$ ,  $-CH=CHCH_2-O-CH_2-$ ,  $-SO_2NR_0-$ ,  $CH_2-$  or  $-CONH-CH_2CH_2-O-CH_2-$ ,  $R_x$  is methyl or hydrogen,  $R_y$  and  $R_z$  are hydrogen,  $h$  is 1,  $x$  is 2,  $d$  is zero, and the  $R_F$  group is saturated, contains 4-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group.

Also preferred are compounds wherein  $R_x$  is a direct bond,  $-CH_2-$ ,  $-CH_2CH_2-O-CH_2-$ ,  $-CH_2CH_2-S-CH_2-$ ,  $-CH=CHCH_2-O-CH_2-$ ,  $-SO_2NR_0-$ ,  $CH_2-$  or  $-CONH-CH_2CH_2-O-CH_2-$ ,  $R_x$  is methyl or hydrogen,  $R_y$  and  $R_z$  are hydrogen,  $h$  and  $d$  are 1,  $x$  is zero,  $D$  is  $-CH_2CH_2-O-CH_2CH_2-$  or pentaerythritol diacetate or dipropionate and the  $R_F$  group is saturated, contains 4-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group.

Most preferably,  $R_1$  is  $-CH_2-$ ,  $R_x$ ,  $R_y$  and  $R_z$  are hydrogen,  $h$  is 1,  $x$  and  $d$  are zero and  $R_F$  is a fully fluorinated, linear perfluoroalkyl group with 4 to 14 carbon atoms.

It is understood that the  $R_F$  group usually represents a homologous mixture of perfluoroalkyl moieties. That is, an  $R_F$  group indicated as containing a certain number of carbon atoms will also contain a small fraction of perfluoroalkyl groups with fewer carbon atoms and a small fraction of perfluoroalkyl groups with a higher number of carbon atoms. Ordinarily, the perfluoroalkyl group preferably contains a mixture of  $C_4F_9-$ ,  $C_6F_{13}-$ ,  $C_8F_{17}-$ ,  $C_{10}F_{21}-$ ,  $C_{12}F_{25}-$  and  $C_{14}F_{29}-$  radicals.

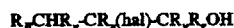
The novel diols of this invention where  $x$  is 0 are made by reaction of an  $R_F-R_1$ -substituted epoxide with  $Na_2S$  or  $NaHS$ , resulting in thioether diols, with elemental sulfur,  $Na_2S_4$  or  $Na_2S_3$  to form polysulfide diols, or with an organic dithiol to form di-thioether diols. Sulfoxides and sulfones ( $x$  is 1 or 2) can be prepared by oxidizing the corresponding thioethers with, for example, 1 or 2 equivalents of an oxidizing agent, preferably a peroxide, per sulfide linkage.

The diol-forming reaction is advantageously carried out in the presence of water and an organic diluent or solvent. Said organic diluent or solvent should be low boiling enough to be recoverable by distillation, including vacuum distillation, if desired. Typical useful diluents and solvents are ketones, such as methyl propyl ketone, methyl ethyl ketone or acetone; esters such as ethyl acetate or isopropyl acetate, and alcohols such as ethanol, n-propanol, isopropanol, n-, sec- or tert.-butanol or allyl alcohol. Typical reaction temperatures are 40° to 80° C. and reaction times are 1 to 8 hours.

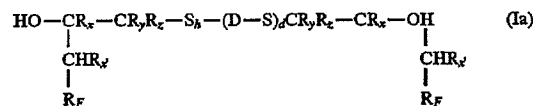
Typical  $R_F$ -epoxides are of the formula  $R_F-R_1-EP$ , wherein  $EP$  denotes an epoxy group,  $-CH(-O-)-CH_2-$ , and  $R_F$  and  $R_1$  are defined as above. Said compounds are known per se or can be prepared by known methods. For example some such epoxides are described in U.S. Pat. Nos. 4,038,195; 4,435,330; 4,490,304 and 4,577,036.

Preferred are epoxides of the formulae  $R_F-EP$ ;  $R_F-CH_2-EP$ ;  $R_F-CH_2CH_2-S-CH_2-EP$ ;  $R_F-CH_2CH_2-O-CH_2-EP$ ,  $R_F-CH=CHCH_2-O-CH_2-EP$ ,  $R_F-SO_2NR_0-CH_2-EP$ ,  $R_F-CONH-CH_2CH_2-O-CH_2-EP$ , with  $R_F-CH_2-EP$  being the most preferred.

It has been unexpectedly found that, instead of making the novel di- $R_F$ -diols from alpoxydes, the halohydrin precursors of the formula



can be used, wherein  $R_y$ ,  $R_x$ ,  $R_z$  and  $R_z$  are hydrogen or  $C_1-C_3$ alkyl, and  $hal$  is bromide or iodide, preferably iodide. The synthesis of diols of the formula Ia



wherein  $R_F$ ,  $R_y$ ,  $R_x$ ,  $R_z$ ,  $h$  and  $d$  are as defined above, by reaction of



wherein  $hal$  is bromide or iodide, with  $Na_2S$ ,  $Na_2S_4$  or an organic dithiol of the formula  $HS-D-SH$ , wherein  $D$  is defined as above, in a basic aqueous medium, is thus another embodiment of this invention. Suitable bases for the basic aqueous medium are alkali metal hydroxides such as sodium and potassium hydroxide.

In the preferred halohydrins,  $R_y$  and  $R_z$  are hydrogen or methyl,  $R_y$  and  $R_z$  are hydrogen and  $hal$  is iodine, with  $R_y$  and  $R_z$  also as hydrogen being most preferred.

The most preferred di- $R_F$ -diol is heptane-1,7-di-perfluoroalkyl-4-thia-2,6-diol. It can be prepared in one reactor by 1) addition of an  $R_F$ -iodide to allyl alcohol to form the iodohydrin, followed by 2) reaction of the iodohydrin with a sulfide. The epoxide of the formula  $RF-CH_2-EP$  is formed in low concentrations as an intermediate during the second step, but does not accumulate as an isolatable compound and is not present in the reaction product. The process of making the preferred diols by reaction of 2 moles of a 2-iodo-3-perfluoroalkyl-1-propanol with one mole of a sulfide is another embodiment of this invention.

The addition of an  $R_F$ -iodide to allyl alcohol to give an iodohydrin intermediate proceeds readily in the presence of a free radical initiator such as an azo compound or a peroxide at conventional initiation temperatures of 35° to 150° C. It was found, however, that only in the presence of small amounts of aqueous solutions of sulfite, bisulfite or dithionite ions does the reaction proceed fast enough and are conversions high enough to make the synthesis commercially practical. This novel process to make the  $R_F$ -iodide-allyl alcohol iodohydrin intermediate and other related compounds is described separately in copending application Ser. No. 08/420,386, now U.S. Pat. No. 5,585,517.

Solvents can be present during this step; for example ketones such as acetone, methyl ethyl ketone or methyl propyl ketone, esters such as isopropyl acetate, alcohols such as ethanol or butanol, ethers such as dioxane or di-(2-hydroxyethyl)-ether, hydrocarbons such as toluene or octane, amides such as dimethylformamide and lactams such as N-methylpyrrolidone.

In the second step the iodohydrin intermediate, a 2-iodo-3-perfluoroalkyl-1-propanol, is reacted with  $Na_2Sx9H_2O$  in the presence of water and an organic diluent or solvent to give a heptane-1,7-di-perfluoroalkyl-4-thia-2,6-diol. Typical diluents and solvents are ketones, such as methyl propyl ketone, methyl ethyl ketone or acetone; esters such as ethyl acetate or isopropyl acetate; alcohols such as ethanol, n-propanol, isopropanol, n-, sec- or tert. butanol or allyl alcohol. Preferably the same solvent is used as for the previous step. Typical reaction temperatures are 40° to 80° C. and reaction times are 1 to 8 hours.

The key step is the in-situ preparation of a 3-perfluoroalkyl-1,2-epoxypropane as a transitory, non-isolatable intermediate. Evidence of a 3-perfluoroalkyl-1,2-epoxypropane being an intermediate is shown in Example 2. In said example, a 3-perfluoroalkyl-1,2-epoxypropane is converted to heptane-1,7-di-perfluoroalkyl-4-thia-2,6-diol using  $Na_2Sx9H_2O$ . The same novel diols can also be prepared by the addition of  $NaHS$  to a 2-iodo-3-perfluoroalkyl-1-propanol.

Instead of allyl alcohol, methallyl alcohol or crotyl alcohol can be used to prepare analogous diols of the formula Ia.

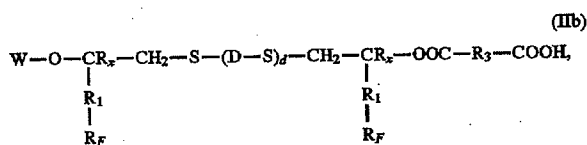
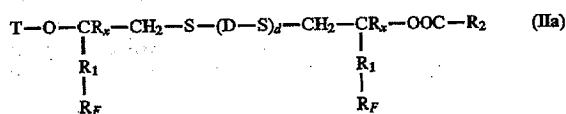
Disulfides and polysulfides of formula (I) can be prepared from the reaction of  $\text{Na}_2\text{S}$  plus elemental sulfur or just elemental sulfur with an  $\text{R}_F$ -iodide at elevated temperatures.  $\text{Na}_2\text{S}_4$  and/or  $\text{Na}_2\text{S}_5$  may also be utilized. These reagents will give a mixture of sulfide and polysulfide structures of formula I, ranging from 1 to 4 sulfur atoms in the cross linkage.

The sulfides and polysulfides of formula I may be oxidized to the corresponding sulfoxides and polysulfoxides or to sulfones and polysulfones. This functional group transformation may be accomplished by the addition of one equivalent of an oxidizing agent, preferably a peroxide, per sulfide linkage or two or more equivalents to give, respectively, sulfoxide/polysulfoxide or sulfone/polysulfone structures of formula I.

Di-thioether diols of formula I can be prepared by reaction of a 2-iodo-3-perfluoroalkyl-1-propanol or an  $\text{R}_F$ -substituted epoxide with a dithiol, for example dimer-captoethylene or pentaerythritol dimercaptpropionate.

The diols of formula I can be further reacted with isocyanates to form urethanes; diisocyanates to form polyurethanes; with carboxylic, sulfuric or phosphoric acids or derivatives to form carboxylate esters, sulfate esters, phosphate esters, or carbonates, respectively. Use of these reaction products and their further derivatives impart oil and water repellency to materials such as glass, wood, paper, leather, textiles such as wool, cotton, polyester and other substrates is another object of this invention.

Useful esters are mono- and diesters of the formula IIa or IIb



wherein  $\text{R}_F$ ,  $\text{R}_1$ ,  $\text{R}_x$ ,  $\text{D}$ , and  $d$  are defined as above,  $\text{T}$  is hydrogen or  $\text{R}_2-\text{CO}-$ , where  $\text{R}_2$  is  $\text{C}_1-\text{C}_{20}$ alkyl,  $\text{C}_6-\text{C}_{14}$ aryl or  $\text{C}_7-\text{C}_{16}$ aralkyl, each of which is unsubstituted or substituted by one or more hydroxy, thiol, carboxyl or  $\text{C}_1-\text{C}_4$ alkyl ester groups and  $\text{W}$  is hydrogen or  $\text{HOOC}-\text{R}_3-\text{CO}-$ , where  $\text{R}_3$  is a direct bond, an alkylene of 1-16 carbon atoms, an arylene of 6 to 14 carbon atoms or an alkarylene of 7 to 16 carbon atoms, which alkylene, arylene or alkarylene is unsubstituted or substituted by  $\text{C}_1-\text{C}_4$ alkyl, chlorine or bromine.

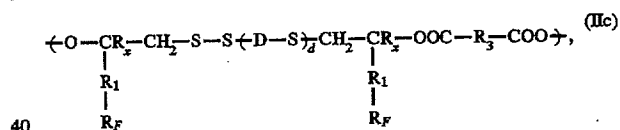
Structurally,  $\text{R}_2$  is the radical residue of a carboxylic acid of the formula  $\text{R}_2-\text{COOH}$ . Typical examples of  $\text{R}_2-\text{COOH}$  include acetic, benzoic, hydroxybenzoic, acrylic, methacrylic, thioacetic and thiopropionic acids and the  $\text{C}_1-\text{C}_4$ alkyl monoesters of terephthalic, phthalic, citric, maleic, fumaric, itaconic, malonic, succinic and thiosuccinic acids.

Preferred esters of the formula IIa are those wherein  $\text{R}_1$  is a direct bond,  $-\text{CH}_2-$ ,  $-\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}_2\text{CH}_2-\text{O}-$

$\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2-$ ,  $-\text{CH}=\text{CHCH}_2-\text{O}-$ ,  $\text{CH}_2-$ ,  $-\text{SO}_2\text{NR}_o-\text{CH}_2-$  or  $-\text{CONH}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2-$ , wherein  $\text{R}_o$  is hydrogen or an alkyl group with 1 to 4 carbon atoms,  $\text{R}_x$  is hydrogen or methyl,  $d$  is zero,  $\text{R}_2-\text{CO}-$  is the radical of acetic, benzoic, hydroxybenzoic, acrylic, methacrylic, thio-acetic or thio-propionic acid, or a  $\text{C}_1-\text{C}_4$ alkyl monoester of terephthalic, phthalic, citric, maleic, fumaric, itaconic, malonic, succinic or thiosuccinic acid and  $\text{R}_F$  is saturated, contains 6-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group. Of these, monomaleates and monosuccinates and mono-ortho- and terephthalates of the formula IIa, especially those wherein  $\text{R}_1$  is  $-\text{CH}_2-$  and  $\text{R}_x$  is hydrogen are especially preferred.

Structurally,  $\text{R}_3$  is the divalent radical residue of a dicarboxylic acid of the formula  $\text{HOOC}-\text{R}_3-\text{COOH}$ . Such dicarboxylic acids include oxalic, maleic, fumaric, malonic, succinic, glutaric, itaconic, adipic, pimelic, suberic, azelaic, sebacic, brassylic, octadecanedioic, dimer acid, 1,4-cyclohexanedicarboxylic, 4,4'-dicyclohexyl-1,1'-dicarboxylic, phthalic, isophthalic, terephthalic, methylphthalic, chlorophthalic, diphenyl-2,2'-dicarboxylic, diphenyl-4,4'-dicarboxylic, 1,4-naphthalene dicarboxylic, diphenylmethane-2,2'-dicarboxylic, diphenylmethane-3,3'-dicarboxylic, diphenylmethane-4,4'-dicarboxylic acid and the like. Also included are compounds wherein  $\text{R}_3$  is substituted by one or two carboxy groups and is derived, for example, from trimellitic anhydride, pyromellitic dianhydride or benzophenone tetracarboxylic acid dianhydride. Compounds of the formula IIb wherein  $\text{R}_3$  is the divalent radical residue of maleic, succinic or adipic acid are preferred.

Also useful are polyesters containing units of the formula IIc



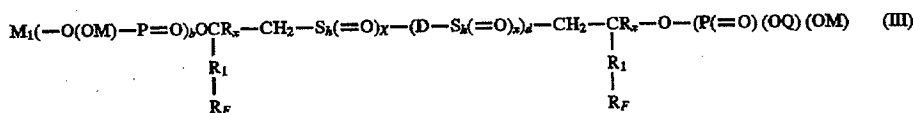
wherein  $\text{R}_F$ ,  $\text{R}_x$ ,  $\text{R}_1$ ,  $\text{R}_3$ ,  $\text{D}$ , and  $d$  are defined as above.

Preferably the polyesters of the formula IIc have molecular weights from about 3,000 to 30,000.

Preferred esters of the formulae IIb and IIc are those wherein  $\text{R}_1$  is a direct bond,  $-\text{CH}_2-$ ,  $-\text{CH}(\text{CH}_3)-$ ,  $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2-$ ,  $-\text{CH}=\text{CHCH}_2-\text{O}-\text{CH}_2-$ ,  $-\text{SO}_2\text{NR}_o-\text{CH}_2-$  or  $-\text{CONH}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2-$ , wherein  $\text{R}_o$  is hydrogen or an alkyl group with 1 to 4 carbon atoms,  $\text{R}_x$  is hydrogen or methyl,  $d$  is zero, and  $\text{R}_F$  is saturated, contains 6-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group. Of these, esters wherein  $\text{R}_1$  is  $-\text{CH}_2-$ ,  $\text{R}_x$  is hydrogen,  $-\text{OOC}-\text{R}_3-\text{COO}-$  is the diradical of maleic, succinic, or adipic acid and  $\text{R}_F$  is a fully fluorinated, linear perfluoroalkyl group with 4 to 14 carbon atoms are especially preferred.

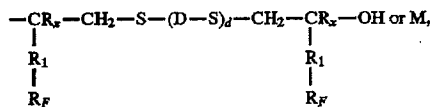
Also useful are carbonates derived from a bischloroformate, e.g. ethylene glycol bischloroformate.

Useful phosphates are of the formula III



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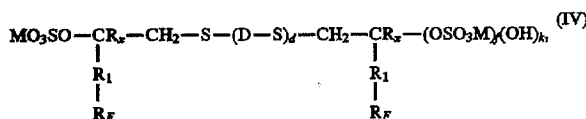
wherein Q is



b is one or zero, M and M<sub>1</sub> are hydrogen, ammonium, C<sub>1</sub>-C<sub>3</sub>alkyl- or C<sub>1</sub>-C<sub>3</sub>hydroxyalkyl-substituted ammonium or an alkali metal cation, and R<sub>F</sub>, R<sub>1</sub>, R<sub>x</sub>, D and d are defined as above, with the proviso that when b is zero, M<sub>1</sub> is hydrogen.

Preferred are phosphates wherein R<sub>1</sub> is a direct bond,  $\text{---CH}_2\text{---}$ ,  $\text{---CH(CH}_3\text{)---}$ ,  $\text{---CH}_2\text{CH}_2\text{---O---CH}_2\text{---}$ ,  $\text{---CH}_2\text{CH}_2\text{---S---CH}_2\text{---}$ ,  $\text{---CH=CHCH}_2\text{---O---CH}_2\text{---}$ ,  $\text{---SO}_2\text{NR}_0\text{---CH}_2\text{---}$  or  $\text{---CONH---CH}_2\text{CH}_2\text{---O---CH}_2\text{---}$ , wherein R<sub>0</sub> is hydrogen or an alkyl group with 1 to 4 carbon atoms, d is zero, R<sub>x</sub> is hydrogen or methyl and R<sub>F</sub> is saturated, contains 6-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group. Especially preferred are phosphates wherein R<sub>1</sub> is  $\text{---CH}_2\text{---}$ , R<sub>x</sub> is hydrogen and R<sub>F</sub> is a fully fluorinated, linear perfluoroalkyl group with 4 to 14 carbon atoms.

Useful sulfates are of the formula IV

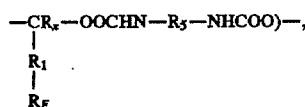
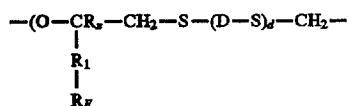


wherein one of f and k is zero and the other is 1, and M, R<sub>F</sub>, R<sub>1</sub>, R<sub>x</sub> d and D are defined as above.

Preferred are sulfates wherein R<sub>1</sub> is a direct bond,  $\text{---CH}_2\text{---}$ ,  $\text{---CH(CH}_3\text{)---}$ ,  $\text{---CH}_2\text{CH}_2\text{---O---CH}_2\text{---}$ ,  $\text{---CH}_2\text{CH}_2\text{---S---CH}_2\text{---}$ ,  $\text{---CH=CHCH}_2\text{---O---CH}_2\text{---}$ ,  $\text{---SO}_2\text{NR}_0\text{---CH}_2\text{---}$  or  $\text{---CONH---CH}_2\text{CH}_2\text{---O---CH}_2\text{---}$ , wherein R<sub>0</sub> is hydrogen or an alkyl group with 1 to 4 carbon atoms, k is 1, d and f are zero, D is  $\text{---CH}_2\text{CH}_2\text{---O---CH}_2\text{CH}_2\text{---}$  or pentaerythritol diacetate or dipropionate, R<sub>x</sub> is hydrogen or methyl and the R<sub>F</sub> group is saturated, contains 4-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group. Especially preferred are sulfates wherein R<sub>1</sub> is  $\text{---CH}_2\text{---}$ , R<sub>x</sub> is hydrogen, d and f are zero and R<sub>F</sub> is a fully fluorinated, linear perfluoroalkyl group with 4 to 14 carbon atoms.

Useful urethanes are the reaction products of a diol of the formula I with an isocyanate of the formula R<sub>4</sub>-NCO, wherein R<sub>4</sub> is the monovalent hydrocarbon radical of phenyl isocyanate, m-isopropenyl-methyl benzyl isocyanate (TMI), 2-isocyanatoethyl acrylate or methacrylate (IEM) or 1,1-dimethyl-2-isocyanatoethyl-m-isopropenylphenyl.

Useful polyurethanes consist of or contain repeating units of the general formula V



wherein R<sub>F</sub>, R<sub>x</sub>, R<sub>5</sub>, D and d are defined as above, and R<sub>5</sub> is the diradical residue of a diisocyanate of the formula OCN-R<sub>5</sub>-NCO.

Preferred polyurethanes are those wherein R<sub>1</sub> is a direct bond,  $\text{---CH}_2\text{---}$ ,  $\text{---CH(CH}_3\text{)---}$ ,  $\text{---CH}_2\text{CH}_2\text{---O---CH}_2\text{---}$ ,  $\text{---CH}_2\text{CH}_2\text{---S---CH}_2\text{---}$ ,  $\text{---CH=CHCH}_2\text{---O---CH}_2\text{---}$ ,  $\text{---SO}_2\text{NR}_0\text{---CH}_2\text{---}$  or  $\text{---CONH---CH}_2\text{CH}_2\text{---O---CH}_2\text{---}$ , wherein R<sub>0</sub> is hydrogen or an alkyl group with 1 to 4 carbon atoms, R<sub>x</sub> is hydrogen or methyl and d is zero, and the R<sub>F</sub> group is saturated, contains 4-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group and the group R<sub>5</sub> is aromatic, aliphatic or cycloaliphatic.

Useful aromatic diisocyanates include toluene diisocyanate CDD (all isomers), 4,4'-diphenylmethane diisocyanate (MDD), tolidine diisocyanate, dianisidine diisocyanate, m-xylylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methyl-isocyanatophenyl)methane-4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 1-nitrophenyl-3,5-diisocyanate, 4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl-methane, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanato-diphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 1,2-naphthalene diisocyanate, 4-chloro-1,2-naphthalene diisocyanate, 4-methyl-1,2-naphthalene diisocyanate, 1,5-naphthalene diisocyanate, 1,6-naphthalene diisocyanate, 1,7-naphthalene diisocyanate, 1,8-naphthalene diisocyanate, 4-chloro-1,8-naphthalene diisocyanate, 2,3-naphthalene diisocyanate, 2,7-naphthalene diisocyanate, 1,8-dinitro-2,7-naphthalene diisocyanate, 1-methyl-2,4-naphthalene diisocyanate, 1-methyl-5,7-naphthalene diisocyanate, 6-methyl-1,3-naphthalene diisocyanate and 7-methyl-1,3-naphthalene diisocyanate.

Useful aliphatic or cycloaliphatic polyisocyanates include 1,2-ethane diisocyanate, propylene-1,2- and -1,3 diisocyanate, 1,4-tetramethylene diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, 1,8-octane diisocyanate, 1,10-decane diisocyanate, 1,12-dodecane, 1,16-hexadecane diisocyanate and other aliphatic diisocyanates such as 1,3-cyclohexane diisocyanate and 1,4-cyclohexane diisocyanate.

Additionally, the following diisocyanates are particularly preferred because urethane compositions made therefrom tend to be non-yellowing: 1,6-hexamethylene diisocyanate (HDI), 2,2,4- and 2,4,4-trimethyl-1,6-diisocyanatohexane (TMDI), dimer acid-derived diisocyanate (DDI), obtained from dimerized fatty acids such as linoleic acid, 4,4'-dicyclo-hexylmethane diisocyanate (hydrogenareal MDI), isophorone diisocyanate, 3-isocyanato-methyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate (LDIM), bis(2-isocyanatoethyl) fumarate (FDI), bis(2-isocyanatoethyl) carbonate and m-tetramethyl-xylylene diisocyanate (TMXDI).

Especially preferred are polyurethanes wherein R<sub>1</sub> is  $\text{---CH}_2\text{---}$ , R<sub>x</sub> is hydrogen, d is zero, and R<sub>F</sub> is saturated and contains 6-18 carbon atoms, is fully fluorinated and contains

at least one terminal perfluoromethyl group, and  $R_2$  is the diradical residue of isophorone diisocyanate, 2,2,4(2,4,4)-trimethyl-1,6-diisocyanatohexane, linoleic dimer acid-derived diisocyanate, 1,6-hexamethylene diisocyanate or 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate.

It is preferred that the polyurethanes have molecular weights from about 3,000 to 30,000.

Esters of the formulae IIa-IIc and carbonates may be prepared by reacting diols of formula I with acid chlorides, esters or chloroformates to yield carboxylate esters and carbonates respectively. For example, acetyl chloride can be reacted with a diol of formula I to give an acetate derivative. This reaction is preferably carried out in the presence of an organic amine to scavenge HCl.

Sulfate esters are prepared by the reaction of the inventive diols with chlorosulfonic acid or, preferably, with sulfamic acid in the presence of a base or a basic solvent such as pyridine, N-methylpyrrolidone, urea or tetramethylurea. This reaction is usually carried out at about 100°–105° C. for 2 to 10 hours. The advantage of using sulfamic acid rather than chlorosulfonic acid is the direct formation of an ammonium salt in a single step.

The reaction of a diol of formula I with polyphosphoric acid or  $\text{POCl}_3$  will give a phosphate ester of the formula III. This reaction is typically carried out at about 85° C. using glyme as solvent. These phosphates are usually reacted with a base such as ammonia to convert them to the corresponding ammonium salts for water solubility and for application testing.

Polyurethanes are prepared from the diols of this invention by the known methods of polyurethane chemistry. These polyurethanes may also contain other building blocks derived from commercially available diols or diamines, especially tertiary amino group-containing diols such as N-methyldiethanolamine, polyethylene oxide diols and 3-aminopropyl-terminated polyethylene oxide (Jeffamine-ED, from TEXACO Corp.), poly-(dimethylsiloxane)-dialkanols and poly-(dimethylsiloxane)-dialkylamino. Typical polyurethane compositions incorporating known diols and diamines in combination with certain other perfluoroalkyl-substituted diols are described for example in U.S. Pat. Nos. 3,968,066, 4,046,944 and 4,098,742.

Also, this invention relates to a substrate containing 0.01 to 10% by weight of a fluorine-containing composition, at least part of said fluorine being provided by one or more compounds derived from an  $R_F$ -diol of formula I. Such substrates include glass, wood, paper, leather, textiles such as nylon, wool, cotton, polyester, and other substrates. The above reaction products and their further derivatives of the diols of formula I impart oil and water repellency to said substrates. Said substrates and methods of preparing them are further objects of this invention.

The following examples are intended for illustrative purposes only, and are not intended to restrict the scope of the invention in any way.

#### Example 1

Synthesis of a 2-iodo-3-perfluoroalkyl-1-propanol.

Into a 1 l round-bottomed flask equipped with condenser, thermometer, stirrer and a nitrogen gas inlet tube are charged 606.0 g (1.0 mole) of a perfluoroalkyl iodide ( $R_F\text{I}$ ) with a homologue distribution of 1.7%  $\text{C}_6$ , 49.8%  $\text{C}_8$ , 33.5%  $\text{C}_{10}$ , 11.1%  $\text{C}_{12}$ , 3.1%  $\text{C}_{14}$ , 0.69%  $\text{C}_{16}$  and 0.16%  $\text{C}_{18}$  (Telomer-AN, from DuPont), 22.6 g  $\text{H}_2\text{O}$  (1.26 mole) and 14.8 g sodium metabisulfite ( $\text{Na}_2\text{S}_2\text{O}_5$ , 0.078 mole). The mixture is heated on an oil bath to 80° C. with stirring. After the

addition of 2.88 g (0.015 mole) 2,2'-azo-bis-(2-methylbutyronitrile) (VAZO-67, from WAKO Chem. Co.), 112.8 g allyl alcohol (1.16 mole) as a 60% solution in water are continuously added over 210 minutes using a Masterflex pump at a flow rate of 32.2 g/h. A small temperature increase of the reaction mass is observed. Product formation was followed by monitoring the decrease of  $R_F\text{I}$  concentration via gas chromatography. No substantial accumulation of  $R_F\text{I}$  is seen, i.e. the allyl alcohol reacts immediately upon addition.

After 210 minutes, the addition rate of the aqueous allyl alcohol solution is increased to 102 g/h for the following two hours. The total amount of allyl alcohol solution used in the reaction is 318.2 g, corresponding to a molar ratio of  $R_F\text{I}$  to allyl alcohol=1.0:3.28. The total amount of water used is 31.5%, based on  $R_F\text{I}$ .

The formed 2-iodo-3-perfluoroalkyl-1-propanol is obtained as a solution in the excess of aqueous allyl alcohol. The excess allyl alcohol is distilled off in vacuo and the product is filtered off, rinsed with deionized water and dried in vacuo at 50° C. It is obtained as a dark-yellow waxy solid in 98% yield; the conversion of  $R_F\text{I}$  is 100%.

#### Example 2

Heptane-1,7-di-perfluoroalkyl-4-thia-2,6-diol.

Into a 300 ml, three neck round-bottomed flask are placed the 2-iodo-3-perfluoroalkyl-1-propanol of Example 1 (70 g, 0.105 mol), 26 g water, 17 g ethanol and 8.6 g methyl propyl ketone (MPK). The mixture is stirred at 42° C. and solid  $\text{Na}_2\text{Sx9H}_2\text{O}$  (126 g, 0.053 mol) is added over a 30 minute period. After the addition is completed, the reaction mixture is heated to 55° C. The progress of the reaction is monitored by gas chromatography. After one hour the reaction is complete. The MPK is distilled off at 80° C., whereupon the mixture separates into two phases. The aqueous phase is removed and the organic phase is washed twice with 10% HCl. Small amounts of residual MPK are removed under vacuum. A light yellow crystalline material is obtained and dried in vacuum (45° C.) to give 110 g (95% yield) of the tide di- $R_F$ -diol with a melting point, m.p., of 118° C.

The structure is confirmed by H-NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  4.3 (2H, bs,  $-\text{CHOH}$ ), 2.7 and 2.9 (4H, m,  $-\text{CH}_2\text{S}-$ ) and 2.4 (4H, m,  $R_F\text{CH}_2-$ ).

#### Example 3

Heptane-1,7-di-perfluoroalkyl-4-thia-2,6-diol; preparation from a perfluoroalkyl-propylene oxide.

Into a 2 l three-neck round-bottomed flask equipped with a mechanical stirrer are poured melted  $\text{C}_9\text{-C}_{21}$ -perfluoroalkyl-propylene oxide (ZONYL-TE; DuPont Chem. Corp.) (559.0 g, 0.98 mol) and 38 ml acetone. This mixture is stirred at 43° C. until it turns clear. To this mixture is added a solution of  $\text{Na}_2\text{Sx9H}_2\text{O}$  (120.1 g, 0.49 mol) in 135 ml water over a 50 minute period. During the addition the temperature of the reaction mixture is maintained at about 43° C. by using a cooling bath. After the addition of  $\text{Na}_2\text{Sx9H}_2\text{O}$  is complete, the stirred yellow turbid mixture is heated at 55° C. for 2 hours. The progress of the reaction is monitored by gas chromatography. After 2 hours the reaction is complete. Acetone is removed from the reaction mixture by distillation at 78° C. and the remaining aqueous slurry is filtered. The filter cake is washed three times with 200 ml of cold water. Subsequent drying of the filter cake under vacuum gives 555.0 g (96.5% yield) of a tan powder with a m.p. of 118°–124° C. and a fluorine content of 63.4%



(Calculated: 63.2%). NMR data are identical to those obtained for Example 2.

#### Example 4

##### Synthesis of a polyurethane.

40.09 g (42.2 mmoles) of the heptane-1,7-di-perfluoroalkyl-4-thia-2,6-diol of Example 2 and 93.04 g isopropyl acetate are placed into a 250 ml 3-necked round-bottomed flask fitted with a mechanical stirrer, gas inlet, thermometer, Dean-Stark trap and condenser. The mixture is kept under nitrogen and heated to reflux to remove water as an azeotrope with the isopropyl acetate: 20 ml of distillate are collected in the trap.

The contents are cooled to 75° C. and 6.74 g (31.6 mmoles) of 2,2,4-trimethyl-1,6-diisocyanatohexane (TMDI) is added, followed by 0.10 g (0.16 mmoles) of dibutyltin dilaurate (DBTL). The flask contents are stirred for approximately one hour at 80° C., or until the TMDI content is below 0.2% as determined by IR.

15.62 g (26.4 mmoles) of dimer acid diisocyanate (DDI 1410, from Henkel Chemie) and 1.90 g (15.9 mmoles) of N-methyl diethanolamine (NMDEA) are added, followed by 26.2 g isopropyl acetate as a rinse. The mixture is stirred for 2 hours at 80° C. After this time no more NCO groups remain present as determined by IR-spectroscopy. The product polyurethane is obtained as a 40% solution in isopropyl acetate. It contains the diol, TMDI, DDI, and NMDEA in a mol ratio of 4:3:2.5:1.5. On drying, the polyurethane forms a clear tough, highly oil- and water-repellent film.

#### Example 5

The following example demonstrates the usefulness of a novel polyurethane as an oil and water-repellent textile finish.

##### Emulsification:

In 93.8 g water are dissolved 1.87 g Arquad-2C/75 (dicocodimethylammonium chloride, from Akzo Corp.) and 0.63 g Ethoquad 18/25 (methyl-polyoxyethyl(15)-octadecyl ammonium chloride, from Akzo Corp.) to make up the aqueous phase. The polyurethane solution of Example 4 is adjusted to 40% solids with isopropyl acetate, forming the organic phase. Both solutions are heated to 60°–70° C. Then 45 g of the polyurethane solution is added to the aqueous phase while stirring. This mixture is homogenized first with a high-shear stirrer (POLYTRON) for 2 minutes, followed by 2–3 passes through a MICROFLUIDIZER at 5000–7000 psi. The emulsion is then stripped free of organic solvent on a rotary evaporator at reduced pressure.

##### Application:

The polyurethane emulsion is formulated into a pad bath containing 6% by weight of the permanent press resin Permafresh-113B (Sequa Chem. Corp.), 1.2% Catalyst 531 ( $\text{Zn}(\text{NO}_3)_2$ ) and an amount of polyurethane emulsion calculated to result in 0.12% fluorine in the bath. This mixture is applied to cotton fabric at 85% wet pick-up. The fabric is dried for 10 min. at 110° C. and cured for 5 min. at 150° C. The test results are shown in the table. They demonstrate excellent performance, even after repeated washing and drycleaning.

##### TEST METHODS:

The AATCC Water Spray test rating was determined according to Standard Test method 22-1985 of the American

Association of Textile Chemists and Colorists, Volume 61, 1986 (also designated ASTM-D-583-58). Ratings are given from 0 (minimum) to 100 (maximum).

The AATCC Oil Rating was determined according to Standard Test method 118-1983 of the American Association of Textile Chemists and Colorists. Ratings are given from 0 (minimum) to 8 (maximum). A commonly accepted level of repellency for oil-repellent coatings in the United States is an oil repellency of 4.

The Bundesmann test simulates the conditions of a fabric being worn during a heavy rain. In this test water absorption is measured in percent pick-up, (underlined numbers in the following table) and appearance (3 samples), rated from 1 (lowest) to 5 (highest rating).

	TEST RESULTS		
	oil kit	spray	Bundesmann
initial	6	3 × 100	<u>11</u> ; 5, 5, 5
5 × 60° wash	5	3 × 80	<u>23</u> ; 2, 1, 1
1 × dryclean	4	100, 90, 90	<u>27</u> ; 5, 3, 2

#### Example 6

This example illustrates the synthesis of di-perfluoroalkyl sulfate esters by reaction of a heptane-1,7-di-perfluoroalkyl-4-thia-2,6-diol with sulfamic acid.

Into a 100 ml round-bottomed flask are placed the heptane-1,7-di-perfluoroalkyl-4-thia-2,6-diol of Example 2 (19.4 g, 0.0150 mol), sulfamic acid (2.62 g, 0.027 mol) and 5.0 g of tetra-methylurea. This mixture is stirred under nitrogen for 1.5 hours at 103° C. The progress of the reaction and the final degree of sulfation is monitored by a two-phase titration of the forming di-perfluoroalkyl sulfate ammonium salt with benzethonium chloride solution according to the procedure described in "Analysis of Surfactants", Surfactant Sci. Series, Vol. 40, (Marcel Decker Inc., New York, 1992).

The final degree of sulfation, expressed as OH equiv.  $_{initial}$  OH equiv.  $_{final}$  is 0.85.

The product is dissolved in water and used for application tests.

#### Example 7

The following example demonstrates the usefulness of the sulfate ester-acids as oil-repellent paper sizes.

##### SAMPLE PREPARATION AND TESTING:

##### External Size Application:

Samples of the product of Example 6 are diluted to the test application levels with distilled water. The solutions are added to a 4% aqueous solution of paper maker's starch (Stayco M, oxidized starch, from Staley Corp.) and then applied to unsized paper by padding (paper dipped through starch solution, and passed through single nip rollers). The resulting sheets are dried at ambient conditions for 15 minutes, then 3 minutes at 200° F. in an "Emerson Speed Drier" (heated metal plate with canvas cover).

##### Oil Kit Test:

The oil repellency of the surface is determined by using the TAPIUM 557 OIL KIT TEST, which consists of determining which of twelve Castor oil-heptane-toluene mixtures having decreasing surface tension causes penetration to occur within 15 seconds: ratings go from 1 (lowest) to 12.

## Grease Resistance Test:

Grease resistance is determined with the Ralston-Purina RP-2 test for pet food materials; Ralston-Purina Company, Packaging Reference Manual Volume 06 - Test Methods.

In summary; cross-wise creased test papers are placed over a grid sheet imprinted with 100 squares. Five grams of sand are placed in the center of the crease. A mixture of synthetic oil and a dye for visualization is pipetted onto the sand and the samples are maintained at 60° C. for 24 hours. Ratings are determined by the percentage of stained grid segments on at least two samples.

## Internal Size Application and Testing:

Six grams of dry recycled pulp consisting of ≈70% hard-wood and 30% soft-wood are diluted in 289 ml distilled water and thoroughly dispersed in a blender. To this pulp slurry is added a 1% dilution (as is) of the test dispersion in distilled water and mixed in for 5 minutes. Then 6 ml of a 1% aqueous solution of cooked cationic starch is added and mixed together for an additional 5 minutes. To this 24 ml of a 50% (on solids) dilution of a water-repellent adjuvant (Hercon-76, from Nalco Chem. Corp.) are added and mixed in for another 10 minutes. The resulting slurry is diluted with an additional 500 ml of distilled water and mixed again. This mixture is then poured over a 100 mesh wire screen, with a vacuum applied from below which pulls the water from the pulp mixture to form a sheet on the screen. The wet sheet is removed from the screen and dried between another screen and a hard surface at a pressure of approximately 0.4 lb./in<sup>2</sup> at 110° C. for 1½ hours.

## Hot-Oil Test:

One ml of hot (110° C.) corn oil is placed on the paper and the time is noted for penetration to occur (20 min. maximum). Paper made in the same manner as above, including the cationic starch and water repellent adjuvant but without a fluorochemical of this invention, demonstrates an oil kit number of <1. It holds the hot corn oil for less than one minute (begins to penetrate as soon as applied).

The amount of oil absorbed is determined gravimetrically by weighing the paper before and after the hot oil test, after the surface oil has been removed.

The Oil-Kit Test is the same as that for the External Size.

The test results are shown in the following table:

Ex. No. 7	% F	External		Internal Size		
		oil kit	RP-2 test	oil kit	time (min.)	% oil absorbed
Compound of Example 6	0.05	5	2 × 0	3	<3	44
	0.07	7	2 × 0	4	>20	0
	0.10	10	2 × 0	5	>20	0

## Example 8

## Conversion of a sulfur diol to a sulfone.

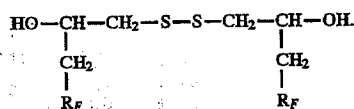
A 100 ml single-necked, round-bottomed flask equipped with a stirring bar and cold water condenser is charged with 19.0 g (0.32 mol) glacial acetic acid and 25.0 g (0.025 mol) of the diol of Example 3. With good stirring, the diol is dissolved by heating to 40° C. and 2.9 g (0.08 mol, 34%)

hydrogen peroxide is added, during which the mixture turns dark amber. After one hour, the reaction mixture is heated to 100° C. and an additional 5.7 g (0.17 mol, 34%) hydrogen peroxide are charged. After 3 hours the product mixture is poured into 1 liter of crushed ice and water, filtered through a Buchner funnel, washed several times with cold water, and dried under vacuum to provide 25.2 g (91%) of tan crystals with a melting point of 125°–128° C.; the structure is confirmed by NMR: (DMF-D<sub>7</sub>, 500 MHz) δ: 5.8 (2H, bs, —OH—), 4.6 (2H, m, —CH(OH)—), 3.2 (4H, m, —C H<sub>2</sub>SO<sub>2</sub>—), 2.8–2.4 (4H, m, —CF<sub>2</sub>CH<sub>2</sub>—).

## Example 9

## Synthesis of a disulfide diol.

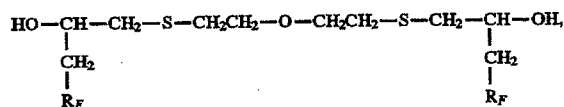
The 2-iodo-3-perfluoroalkyl-1-propanol of Example 1, 13.3 g (26 mmol, in 6 g ethanol) is magnetically stirred in a three-necked round-bottomed flask at 54° C. A solution of 2.4 g (90%, 12.4 mmol) sodium tetrasulfide, 2 g ethanol and 2.3 g water are added through an addition funnel over 30 minutes to give a thick, yellow, paste. After holding for one hour at 54° C., the temperature is raised to 75° C. and held there for 5 hours. GC analysis at this time shows 85% conversion of the 2-iodo-3-perfluoroalkyl-1-propanol. The product mixture is evaporated to dryness and washed with cold, slightly acidic deionized water to give 11.1 g (92%) of a gray solid. Analysis by GC/MS of the crude mixture shows instead of the tetrasulfide the disulfide of the formula:



## Example 10

## Synthesis of a di-thioether diol.

The 2-iodo-3-perfluoroalkyl-1-propanol of Example 1 (10 g, 15 mmol) in 10 g ethanol are magnetically stirred at 49° C. in a 50 ml three-necked, round-bottomed flask. To this solution is added through a dropping funnel over 35 minutes a solution of 1.1 g (95%, 7.5 mmol) di(2-mercaptoethyl) ether, 3.0 g (50%, 1.6 mmol) sodium hydroxide and 4.1 g ethanol to give an off-white paste. Next 5.8 g acetone is added and the solution is stirred at 49° C. for 2 hours, then refluxed at 76° C. for one hour. The product mixture is evaporated to dryness under reduced pressure at 65° C. on a rotary evaporator. The resulting cake is stirred in 500 ml of ice cold diluted HCl (pH < 3), filtered through a Buchner funnel and dried under reduced pressure at 60° C. GC analysis of the yellow solid (8.4 g, 95%, m.p. 95°–107° C.) shows complete conversion of the 2-iodo-3-perfluoroalkyl-1-propanol to product. The structure of the product,

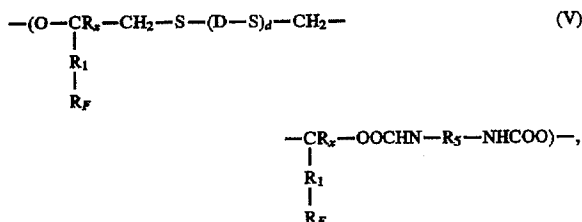


is confirmed by GC/MS.

What is claimed is:

1. A polyurethane having a molecular weight of from about 3,000 to 30,000 which consists of or contains repeating units of the formula V

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wherein

 $R_x$  is hydrogen or methyl, $R_2$  is aromatic, aliphatic or cycloaliphatic

$R_1$  is a direct bond, a linear or branched alkylene of up to 6 carbon atoms, alkyleneoxyalkylene of up to 6 carbon atoms, alkyleneethioalkylene of up to 6 carbon atoms, alkyleneoxy of up to 6 carbon atoms, alkenyleneoxyalkylene of up to 6 carbon atoms, alkyleneethioalkyleneoxyalkylene of up to 9 carbon atoms, carbonamidoalkylene where the alkylene moiety contains up to 6 carbon atoms and the amido nitrogen is unsubstituted or further substituted by lower alkyl, sulfonamidoalkylene wherein the alkylene moiety contains up to 6 carbon atoms and the amido nitrogen is unsubstituted or further substituted by lower alkyl; carbonamidoalkyleneethioalkylene wherein the carbonamidoalkylene moiety is as defined hereinabove and the thioalkylene moiety contains up to 6 carbon atoms, or sulfonamidoalkyleneethioalkylene wherein the sulfonamidoalkylene moiety is as defined hereinabove and the thioalkylene moiety contains up to 6 carbon atoms,  $d$  is 0 or 1,

$D$  is an alkylene group with 2 to 10 carbon atoms, a dialkylene ether group with 4 to 10 carbon atoms, or pentaerythritol diacetate or dipropionate, and

$R_F$  is a monovalent, perfluorinated, alkyl or alkenyl, straight, branched or cyclic, organic radical having 3 to 20 fully fluorinated carbon atoms, which radical can be interrupted by one or more divalent oxygen or sulfur atoms, and each  $R_F$  radical is the same or different.

2. A polyurethane according to claim 1, wherein

$R_1$  is a direct bond,  $\text{---CH}_2\text{---}$ ,  $\text{---CH(CH}_3\text{)---}$ ,  $\text{---CH}_2\text{CH}_2\text{---O---CH}_2\text{---}$ ,  $\text{---CH}_2\text{CH}_2\text{---S---CH}_2\text{---}$ ,  $\text{---CH=CHCH}_2\text{---O---CH}_2\text{---}$ ,  $\text{---SO}_2\text{NR}_6\text{---CH}_2\text{---}$  or  $\text{---CONH---CH}_2\text{CH}_2\text{---O---CH}_2\text{---}$ , wherein  $R_6$  is hydrogen or an alkyl group with 1 to 4 carbon atoms,

 $d$  is zero,

the  $R_F$  group is saturated, contains 4-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group and

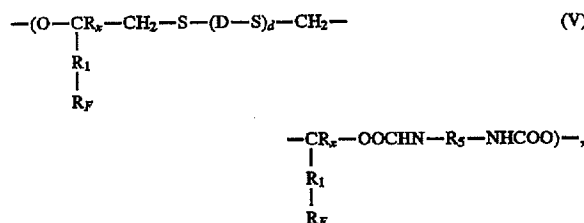
$R_5$  is the diradical residue of a diisocyanate of the formula  $\text{OCN---R}_5\text{---NCO}$  selected from the group consisting of toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, dianisidine diisocyanate, m-xylylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methylisocyanatophenyl)methane-4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 1-nitrophenyl-3,5-diisocyanate, 4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-

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diisocyanatodiphenylmethane, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanato-diphenyl, 1,2-naphthalene diisocyanate, 4-chloro-1,2-naphthalene diisocyanate, 4-methyl-1,2-naphthalene diisocyanate, 1,5-naphthalene diisocyanate, 1,6-naphthalene diisocyanate, 1,7-naphthalene diisocyanate, 1,8-naphthalene diisocyanate, 4-chloro-1,8-naphthalene diisocyanate, 2,3-naphthalene diisocyanate, 2,7-naphthalene diisocyanate, 1,8-dinitro-2,7-naphthalene diisocyanate, 1-methyl-2,4-naphthalene diisocyanate, 1-methyl-5,7-naphthalene diisocyanate, 6-methyl-1,3-naphthalene diisocyanate, 7-methyl-1,3-naphthalene diisocyanate, 1,2-ethane diisocyanate, propylene-1,2- and -1,3 diisocyanate, 1,4-tetramethylene diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, 1,8-octane diisocyanate, 1,10-alecane diisocyanate, 1,12-dodecane diisocyanate, 1,16-hexadecane diisocyanate, 1,3-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), 1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethyl-1,6-diisocyanatohexane, dimer acid-derived diisocyanate obtained from dimerized linoleic fatty acid, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate, bis(2-isocyanatoethyl) fumarate, bis(2-isocyanatoethyl) carbonate and m-tetramethylxylene diisocyanate.

3. A polyurethane according to claim 2, wherein  $R_1$  is  $\text{---CH}_2\text{---}$ ,  $R_x$  is hydrogen,  $d$  is zero, and  $R_F$  is saturated and contains 6-18 carbon atoms, is fully fluorinated and contains at least one terminal perfluoromethyl group, and  $R_5$  is the diradical residue of isophorone diisocyanate, 2,2,4(2,4,4)-trimethyl-1,6-diisocyanatohexane, linoleic dimer acid-derived diisocyanate, 1,6-hexamethylene diisocyanate or 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate.


4. A method of treating a substrate to impart oil and water repellency to it, which comprises applying an effective amount of a fluorine-containing composition thereto, wherein at least part of the fluorine in said composition is provided by one or more compounds selected from the group consisting of polyurethanes having molecular weights of from about 3,000 to 30,000 and consisting of or containing repeating units of the formula V

wherein  $R_F$ ,  $R_x$ ,  $R_2$ ,  $D$ ,  $d$  and  $R_5$  are as defined in claim 1.

\* \* \* \* \*

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## **APPENDIX D**



*Steven S. Zumdahl*

University of Illinois

# CHEMISTRY

Instructor's Edition

Third Edition

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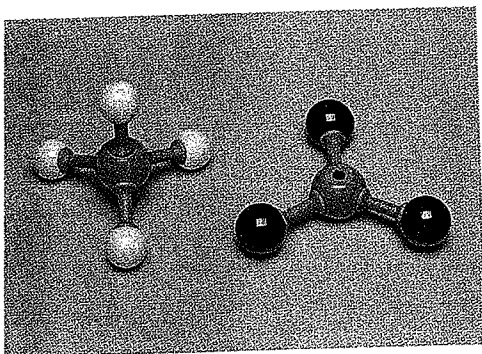
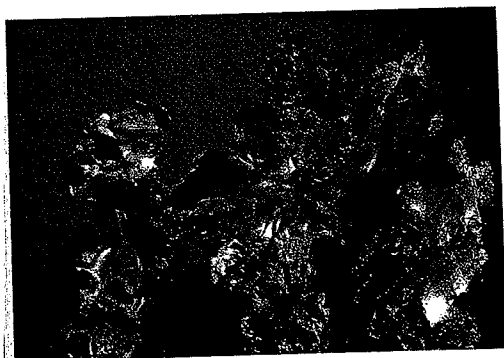


Figure 2.20

Ball-and-stick models of the ammonium ion ( $\text{NH}_4^+$ ) and the nitrate ion ( $\text{NO}_3^-$ ).



Gold is one of only a few metals that occur naturally as a free element, sometimes in spectacular form. The largest gold nugget ever mined in Colorado (found near Breckenridge) weighs 13 pounds.

A solid consisting of oppositely charged ions is called an **ionic solid**, or a **salt**. Ionic solids can consist of simple ions, as in sodium chloride, or of **polyatomic** (many atom) **ions**, as in ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), which contains ammonium ions ( $\text{NH}_4^+$ ) and nitrate ions ( $\text{NO}_3^-$ ). The ball-and-stick models of these ions are shown in Fig. 2.20.

## 2.7 An Introduction to the Periodic Table

### Purpose

- To introduce various features of the periodic table.

In a room where chemistry is taught or practiced, a chart called the **periodic table** is almost certain to be found hanging on the wall. This chart shows all the known elements and gives a good deal of information about each. As our study of chemistry progresses, the usefulness of the periodic table will become more obvious. This section will simply introduce it to you.

A simplified version of the periodic table is shown in Fig. 2.21. The letters in the boxes are the symbols for the elements; these abbreviations are based on the current element names or the original names\* (see Table 2.2). The number shown above each symbol is the **atomic number** (number of protons) for that element. For example, carbon (C) has atomic number 6, and lead (Pb) has atomic number 82. Most of the elements are **metals**. Metals have characteristic physical properties such as efficient conduction of heat and electricity, malleability (they can be hammered into thin sheets), ductility (they can be pulled into wires), and (often) a lustrous appearance. Chemically, metals tend to *lose* electrons to form positive ions. For example, copper is a typical metal. It is lustrous (although it tarnishes readily); it is an excellent conductor of electricity (it is widely used in electrical wires); and it is

Table 2.2

### The Symbols for the Elements that Are Based on the Original Names

Current Name	Original Name	Symbol
Antimony	Stibium	Sb
Copper	Cuprum	Cu
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Mercury	Hydragyum	Hg
Potassium	Kalium	K
Silver	Argentum	Ag
Sodium	Natrium	Na
Tin	Stannum	Sn
Tungsten	Wolfram	W

\*See David W. Ball, "Elemental Etymology: What's in a Name?" *Journal of Chemical Education* 62 (1985): 787.

Alkaline earth metals

1 1A

2 2A

3 4 5 6 7 8 9 10 11 12

Transition metals

13 3A

14 4A

15 5A

16 6A

17 7A

18 8A

Noble gases

Halogens

Alkali metals

\*Lanthanides

†Actinides

**Figure 2.21**

The periodic table. Although rutherfordium and hahnium have been proposed as names for elements 104 and 105, an attempt is being made to name the elements after 103 systematically, using a letter abbreviation for each number. In this system the symbol for element 104 is Unq, and for 105 is Unp. The systematic symbols are shown for elements 106–109.

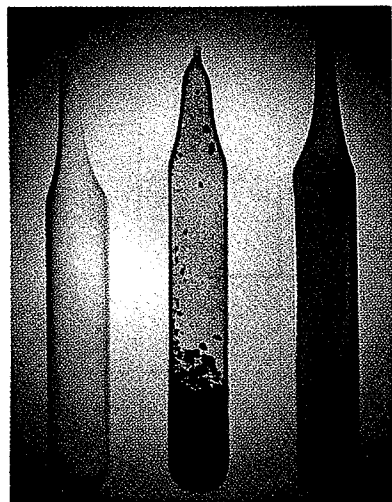
readily formed into various shapes, such as pipes for water systems. Copper is also found in many salts, such as the beautifully blue copper sulfate, in which copper is present as  $\text{Cu}^{2+}$  ions. Copper is a member of the transition metals—the metals shown in the center of the periodic table.

The relatively few **nonmetals** appear in the upper right-hand corner of the table (to the right of the heavy line in Fig. 2.21), except hydrogen, a nonmetal that resides in the upper left-hand corner. The nonmetals lack the physical properties that characterize the metals. Chemically, they tend to *gain* electrons in reactions with metals to form negative ions. Nonmetals often bond to each other by forming

Metals tend to form positive ions;  
nonmetals tend to form negative ions.



Elements in the same vertical column in the periodic table form a group (or family) and generally have similar properties.



Three members of the halogen family: chlorine (green), iodine (purple), and bromine (reddish-brown).

Another format of the periodic table will be discussed in Section 7.11.

covalent bonds. For example, chlorine is a typical nonmetal. Under normal conditions it exists as  $\text{Cl}_2$  molecules; it reacts with metals to form salts containing  $\text{Cl}^-$  ions ( $\text{NaCl}$ , for example); and it forms covalent bonds with nonmetals (for example, hydrogen chloride gas,  $\text{HCl}$ ).

The periodic table is arranged so that elements in the same vertical columns (called **groups** or **families**) have *similar chemical properties*. For example, all the **alkali metals**, members of Group 1A—lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr)—are very active elements that readily form ions with a 1+ charge when they react with nonmetals. The members of Group 2A—beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra)—are called the **alkaline earth metals**. They all form ions with a 2+ charge when they react with nonmetals. The **halogens**, the members of Group 7A—fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At)—all form diatomic molecules. Fluorine, chlorine, bromine, and iodine all react with metals to form salts containing ions with a 1− charge ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ). The members of Group 8A—helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn)—are known as the **noble gases**. They all exist under normal conditions as monatomic (single-atom) gases and have little chemical reactivity.

Note from Fig. 2.21 that alternate sets of symbols are used to denote the groups. The symbols 1A through 8A are the traditional designations, whereas the numbers 1 to 18 have been suggested recently. In this text the 1A to 8A designations will be used.

The horizontal rows of elements in the periodic table are called **periods**. Horizontal row one is called the **first period** (it contains H and He); row two is called the **second period** (elements Li through Ne); and so on.

We will learn much more about the periodic table as we continue with our study of chemistry. Meanwhile, when an element is introduced in this text, you should always note its position on the periodic table.

## 2.8 Naming Simple Compounds

### Purpose

- To demonstrate how to name compounds given their formulas and to write formulas given their names.

When chemistry was an infant science, there was no system for naming compounds. Names such as sugar of lead, blue vitrol, quicklime, Epsom salts, milk of magnesia, gypsum, and laughing gas were coined by early chemists. Such names are called **common names**. As chemistry grew, it became clear that using common names for compounds would lead to unacceptable chaos. Nearly five million chemical compounds are currently known. Memorizing common names for these compounds would be an impossible task.

The solution, of course, is to adopt a *system* for naming compounds in which the name tells something about the composition of the compound. After learning the system, a chemist given a formula should be able to name the compound, or given a

The systematic naming of organic compounds will be discussed in Chapter 22.

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## **APPENDIX E**

# Organic Chemistry

SECOND EDITION

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*University of California, Davis*



W. H. Freeman and Company  
NEW YORK

Cover Image by Tomo Narashima

**About the Cover:** Calicheamicin (*at right*), one of the most potent cancer fighters ever discovered, is shown approaching a strand of DNA, the genetic material of living cells. This anticancer agent has only recently been found in nature. The cover is adapted from a computer-generated image provided by K. C. Nicolaou (The Scripps Research Institute and the University of California, San Diego) and Michael Peak (The Scripps Research Institute).

Calicheamicin acts by undergoing an extraordinary transformation—into a short-lived chemical species called a *radical*, which then attacks the DNA of tumor cells. As you will see in Chapter 8, radicals underlie the course of many organic reactions, including damage to normal cells that promotes aging. Chapter 14 explains in detail the action of calicheamicin and other naturally occurring antibiotics, and Chapter 25 discusses chemical defenses against damage to human cells.

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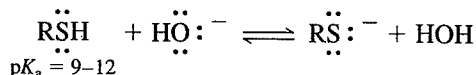
No part of this book may be reproduced by any mechanical, photographic, or electronic process, or in the form of a phonographic recording, nor may it be stored in a retrieval system, transmitted, or otherwise copied for public or private use, without written permission from the publisher.

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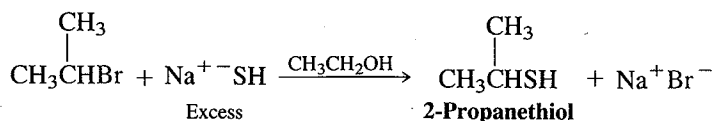
Partly because of the relatively weak S-H bond, thiols are also more acidic than water, with  $pK_a$  values ranging from 9 to 12. They can therefore be more readily deprotonated by hydroxide and alkoxide ions.

#### Acidity of Thiols



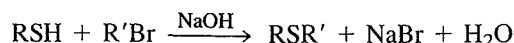
### Thiols and sulfides react much like alcohols and ethers

Many reactions of thiols and sulfides resemble those of their oxygen analogs. The sulfur in these compounds is even more nucleophilic than the oxygen in alcohols and ethers. Therefore, thiols and sulfides are readily made by nucleophilic attack of  $\text{RS}^-$  or  $\text{HS}^-$  on haloalkanes. A large excess of the  $\text{HS}^-$  is used in the preparation of thiols to ensure that the product does not react with the starting halide to give the dialkyl sulfide.

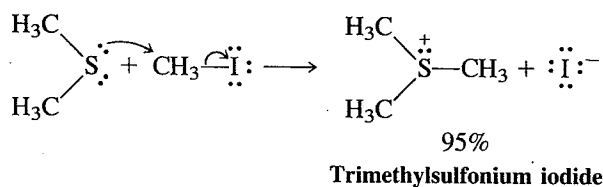


Sulfides are prepared in an analogous way by alkylation of thiols in the presence of base, such as hydroxide. The base generates the alkanethiolate, which reacts with the haloalkane by an  $\text{S}_\text{N}2$  process. Because of the strong nucleophilicity of thiolates, there is no competition from hydroxide in this displacement.

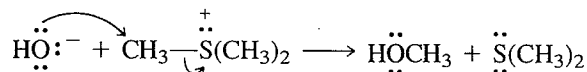
#### Sulfides by Alkylation of Thiols



The nucleophilicity of sulfur also explains the ability of sulfides to attack haloalkanes to furnish **sulfonium ions**.



Like their alkyloxonium analogs, sulfonium salts are subject to nucleophilic attack at carbon, the sulfide functioning as the leaving group.



### EXERCISE 9-22

(a) Sulfide A is a powerful poison known as "mustard gas," a devastating chemical-warfare agent used in the First World War and again in the recent war between Iraq and Iran. Propose a synthesis starting with oxacyclopropane. (b) Its mechanism of